EFFECT OF SOME TRANSITION METAL OXIDE ADDITIVES ON THE FIRED PROPERTIES OF TRI- AXIAL CERAMICS

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Master of Technology

In

Ceramic Engineering

By

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Under the supervision of

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CERTIFICATE

This is to certify that the thesis entitled, **"EFFECT OF SOME TRANSITION METAL OXIDE ADDITIVES ON THE FIRED PROPERTIES OF TRI- AXIAL CERAMICS"**, submitted by **Mr. Snehsh T. S** carried out in **National Institute of Technology, Rourkela**, in partial fulfilment of the requirements for the award of **Master of Technology** Degree in **Ceramic Engineering,** is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree or diploma.

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Snehesh T S

ABSTRACT

A tri-axial ceramic or Porcelain can be defined as a glazed or unglazed vitreous ceramic body made by porcelain process, and used for technical purposes when they are vitreous. Porcelain is distinguished from other whitewares because of the lack of open pores. Porcelain possess properties such as high strength, toughness, low permeability, translucency etc. which makes porcelain useful in various fields of applications such as electrical, mechanical, chemical, structural fields. All these properties possessed by porcelain comes mainly from the mullite and the glassy phase present in the system.

Earlier studies showed that by the addition of mineralizing agents or additives, the reaction rates and the phase formations can be varied. Also most of the transition metal oxide additives showed a higher affinity towards the mullite incorporation and enhancing reaction rates. To the best of our knowledge, there was not much literatures available on the effect of transition metal oxides such as Cr_2O_3, CoO and NiO incorporation in tri-axial systems. Hence the effect of these oxides on the physical and mechanical properties together with phase formation was studied by preparing porcelain batches containing different additive percentages and fired at temperatures 1100^oC, 1200^oC and 1300^oC. It was observed that Cr_2O_3 because of its refractory nature does not help during the reaction stages and hence deterioration of properties was observed, whereas CoO, and NiO enhances the reactions by regulating the viscosity of the melt at certain conditions. These reactions lead to increased secondary mullitization and hence advances in properties such as bulk density, porosity and also mechanical properties obtained. Hence transition metal oxides like CoO and NiO can be used further for applications in different fields requiring higher strength and densities.

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CHAPTER- I

INTRODUCTION

1.1 INTRODUCTION

A whiteware is defined as "a fired ware which may be a glazed or unglazed ceramic body that is commonly white and having fine texture, designating such product classifications as porcelain, china, tile , earthen ware, and semi vitreous ware" [1]. Among these classifications, porcelain is distinguished by its firing temperature, composition and mainly by the lack of open porosities on the fired body.

China is considered as the birth place of porcelain, where in the early 16^{th} centuries porcelain was reported as first prepared. The porcelain of that scenario was mainly used for the preparation of crockeries, vessels and sculptures. Because of the lack of good firing techniques and glazes the porcelain was of poor quality, so the porcelain at that ages were known as primitive porcelain. But as the time passed development of high quality raw materials, improved firing techniques and findings on the use of additives etc. promoted the production of porcelain. Finally porcelain potteries and other products became a major part of the world's daily life. Now a days porcelain is used in every fields of human life starting from the basic potteries to highly advanced and complex applications such as in space shuttles, refractories, structural etc. [2].

By the ASTM definition, porcelain is a vitreous glazed or unglazed ceramic body made from porcelain process, used for technical applications, containing such products as chemical, mechanical, electrical, thermal wares and also in structural applications when they are vitreous [1]. The porcelain have properties such as toughness, whiteness, low permeability, high strength, translucency, hardness, elasticity and resonance. Also high resistance to thermal shock and chemical attacks, which makes porcelain useful in various fields of applications such as electrical, mechanical, chemical, structural , pottery, laboratory equipments, thermal wares and refractories.

Mullite is one the most promising compound present in porcelain bodies and most important in both advanced and conventional ceramics. It possess properties such as good chemical and thermal stability, high melting point, low creep rate, thermal shock resistance, good toughness and strength, low thermal conductivity (k=2$Wm^{-1}K^{-1}$), low thermal expansion coefficient (20/200^{o}C=4*10^{-6} K^{-1}) etc. which makes it one among the most important engineering material [3].

In porcelain bodies two type of mullite formation was reported crystalline mullite with a scaly or flaky structure formed in the clay relict is considered as primary mullite while the long needle shaped mullite formed from silica rich glassy phase derived from the melting of feldspar is secondary mullite. These are also known as type-I and type-II mullite. Sometimes secondary mullite with very high aspect ratio was detected in the region associated with highly fluid matrix those are known as type-III mullite [4]. The needle shaped mullite present in the body has effects on both physical and mechanical properties of fired ceramics. Better strength and toughness in a porcelain body is related with the presence of high aspect ratio mullite [5]. The presence of alkali rich flux, their concentration gradient, diffusion rates impurity content effects the mullite formation [6].

The mullite structure present in a porcelain body is able to incorporate a very large amount of transition metal oxides. The transition metal ions sometimes get into the Al_2O_4 terahedra or otherwise get incorporated with the AlO_6 octahedra of the mullite running parallel to the c-axis by replacing the Al^{3+}, or by getting into the voids generated by the oxygen removal from the octahedral positions. One another possible case was that the ions having larger size and lower valence cannot enter into these sites but they react with the ɤ-Al_2O_3 at lower temperatures (500-

1000ºC) and forms a defective metal alumina spinel structure ($MeAl_2O_4$). Also transition metal oxides like TiO2, Mno2, FeO and CuO showed positive results when added to tri-axial system.

1.2 OBJECTIVE OF THE WORK

A large number of study has been done on the effect of different additive on the mullitization behavior and on the physico-mechanical properties of tri-axial ceramic but no work has been taken out till date on the role of transition metal oxide additive though they have positive effect on mullitization behavior in silica-alumina binary system. So this work was taken to find out the effects of transition metal oxide additives such as Cr_2O_3, NiO and CoO on the fired characteristics of a tri-axial composition. The physical and mechanical properties of the samples together with phase formations and morphology of the formed phases were studied.

CHAPTER- II

LITERATURE REVIEW

2.1. Raw Materials:

A tri-axial body is a combination of clay, quartz and feldspar, because of this three component composition porcelain is known as a tri-axial body. The clay, quartz and feldspar are known as the primary raw materials which forms a porcelain body. Also some of the raw materials which are used with respect to the need are also there, known as the secondary raw materials. The secondary raw materials used may vary with respect to the type of white ware to be produced, some examples are bentonite/montmorillonite, pearlite, glass frits, talc, bone ash, zircon etc.

The primary raw materials are given below.

Raw material	Composition
China clay	$Al_2O_3.2SiO_2.2H_2O$
Ball clay	$Al_2O_3.2SiO_2.2H_2O$
Potash feldspar	$K_2O.Al_2O_3.6SiO_2$
Soda feldspar	$Na_2O.\ Al_2O_3.6SiO_2$
Quartz	SiO_2
Nepheline syenite	$K_2O.3Na_2O.4Al_2O_3.9SiO_2$
Alumina	Al_2O_3

Table; 2.1.1 Primary Raw materials used

2.1(a) Clays

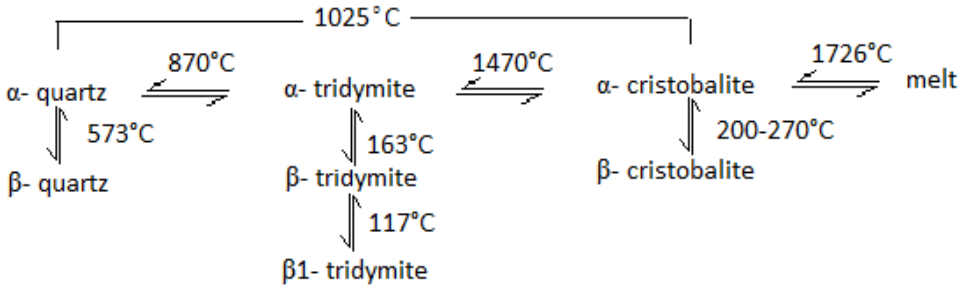
Clay is the most important part among the raw materials, which forms the body of porcelain, provides green strength and plasticity during the porcelain forming stages. About the half part of porcelain body is composed of clay [10]. The clays are of different types and are formed by the decomposition of granite kind of igneous rocks. Among those china clay is the most

important one, which is white and also gives white burning because of the very low impurity content. The common impurities present in china clay are iron and titanium compounds [2]. China clay also possess refractory nature because of the lower impurity levels. Next comes the ball clay, in this also the essential clay mineral is kaolinite. Ball clay is much finer than china clay which gives it more dry strength and higher plasticity. Since it is sedimentary clay contains a large amount of organic impurities and common impurities like iron and titanium it has lower refractoriness and gives fired color [1, 2].

2.1(b) Fillers

The filler materials usually have really high melting temperatures and are chemically resistant at commercial firing temperatures (below 1300^{o}C).they help in reducing the tendency of the body to shrink, distort or warp when fired at temperatures forming high quantity of viscous glass. Most common fillers used for porcelain bodies are quartz and flint, in which dissolution of silica in feldspathic glass is an essential part in its microstructural evolution. On firing it melts and forms a glassy phase which provides the respective bonding strength and forms a dense structure [2]. The fillers have the larger particle size, hence they assist in resisting cracking during firing, prevents pyroplastic deformations by forming a skeletal network and help in reducing viscosity of the slip. Also larger particle size causes a considerable increase in packing density of the green body, reduced shrinkage and increased strength [1]. It was also reported that large quantity of fine grained quartz increases the strength of the body, at the same time some other claimed that lower quartz content provides higher strength [8]. The flint is used in pottery industries, addition of which reduces dry shrinkage and also reduces plasticity. Also kyanite, rice husk ash, sillimanite sand, fly ash, blast furnace slag and fume silica are used as filler materials [34]. Silica exist in three crystalline forms namely quartz, tridymite and cristobalite. All of these possess the same chemical

formula (SiO_2) but differ in the atomic arrangement of silicon and oxygen in the structure. The conversion and inversion reactions occurring during the firing of silica is given below.



Figure; 2.1.1 Conversion and inversion reactions during firing of silica

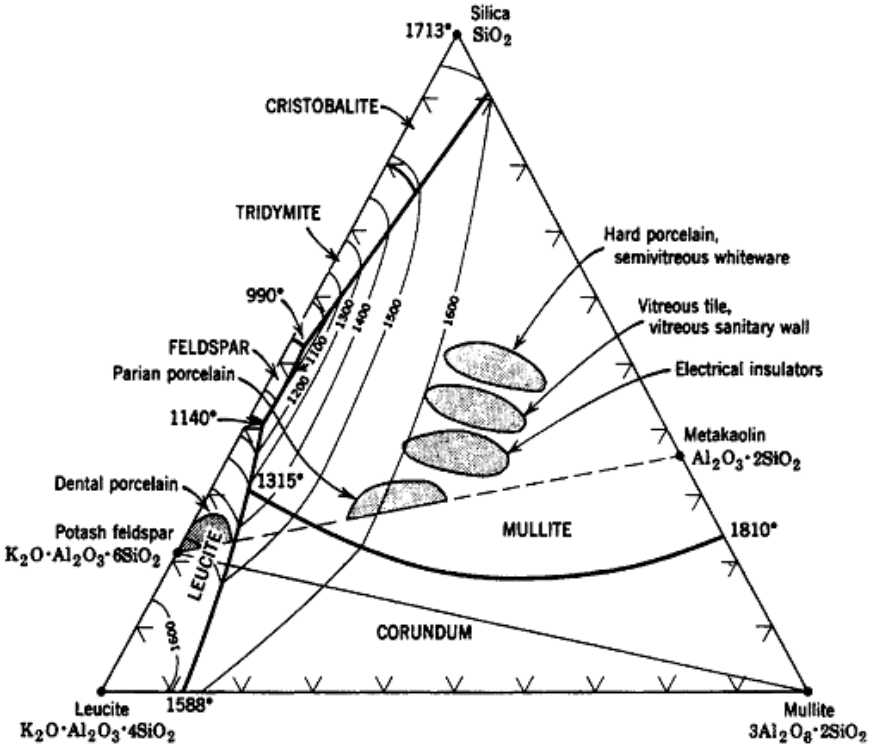
Calcined alumina is also used as filler instead of silica to avoid the quartz inversion, so that the mechanical property is improved. But the higher cost and poor dissolution rate of alumina makes it least used in comparison with silica.

2.1(c) Fluxes

The flux, feldspar is an alkaline aluminosilicate minerals which is used to lower the viscous liquid formation temperatures of the minerals present in the porcelain body. The liquid phase formed reacts with the other constituents present in the body, permeates the microstructure and finally leading to its densification. The flux is composed of about one quarter of the total porcelain batch [10, 21]. Potash feldspar ($K_2O.Al_2O_3.6SiO_2$) are the most extensively used fluxes for porcelain manufacturing, followed by soda feldspar ($Na_2O.Al_2O_3.6SiO_2$) and lime feldspar ($CaO.Al_2O_3.2SiO_2$). Potash feldspar crystallizes into two forms, the monoclinic form is called the orthoclase and the triclinic form known as the microcline. At the same time the lime and soda feldspar crystallize and forms triclinic anorthite and albite respectively. As the feldspar content increases the vitrification temperature of the body decreases [4]. Nephelinesyenite can be

substituted for feldspar commercially, which helps in increasing the alkali level of the glassy phase and in reducing the firing temperature. Nepheline syenite is composed of minerals albite, nepheline and microcline, which possess a higher alkali: silica ratio (4:9) than feldspar (1:6) [1].

Based on the type of application and compositions used, porcelain is of different types. The compositions of various industrial porcelains are graphically represented in the K_2O- Al_2O_3- SiO_2 phase diagram given below.



Figure; 2.1.2 K_2O-Al_2O_3-SiO_2 phase diagram showing different porcelain types[1].

2.2. FIRING AND MICROSTRUCTURAL DEVELOPMENT

Firing is the final and most important stage in the preparation of a porcelain body. The reactions that are occurring during the sintering of a porcelain body are as follows.

(1) At a temperature of about 550°C dehydroxylation occurs, the hydroxyl group present in the kaolinite structure escapes and forms metakaolin ($Al_2O_3\,2SiO_2$).

$$Al_2O_3.2SiO_2.2H_2O \xrightarrow{\sim 550^{\circ}C} Al_2O_3.2SiO_2 + 2H_2O \uparrow$$

(2) By reaching about 573°C quartz inversion starts, α to β quartz inversion is occurred.

(3) Within the temperature of 700°C- 1000°C sanidine is formed. It is a high temperature, homogeneous mixed alkali feldspar and its formation depends on the Na: K ratio.

(4) In the temperature range of 950°C- 1000°C metakaolin is transformed into amorphous silica together with a ɤ- alumina spinel is formed.

$$3(Al_2O_3.2SiO_2) \xrightarrow{\sim 950\text{-}1000^{\circ}C} 0.282Al_8\,(Al_{13.33}{}^{*}{}_{2.66})\,O_{32} + 6SiO_2$$

Or

$$3(Al_2O_3.2SiO_2) \xrightarrow{\sim 950\text{-}1000^{\circ}C} 0.562Si_8\,(Al_{10.67}{}^{*}{}_{5.33})\,O_{32} + 3SiO_2$$

Where the products ($0.282Al_8(Al_{13.33}{}^{*}{}_{2.66})\ O_{32}$) is the gamma alumina spinel and ($0.562Si_8(Al_{10.67}{}^{*}{}_{5.33})\ O_{32}$) is aluminosilicate spinel. The reaction product silica is of amorphous nature and is formed at around 980°C.

(5) In normal porcelain the amorphous silica which is liberated due to the metakaolin decomposition assist in the formation of a eutectic melts at around 990°C.

(6) During the next stages of firing, above 1000°C, a stable form of the aluminosilicate is formed at this high temperature and atmospheric pressure, called the mullite ($3Al_2O_3.2SiO_2$). The mullite formation can be started at 980°C and as the temperature is increasing more mullite phase is

formed. The mullite formation is of two types primary and secondary. The mullite formed because of firing the clay component known as primary mullite (2:1) and the mullite formed as a reaction product of clay component and flux called the secondary mullite (3:2) [10]. The transformation of unstable spinel phase into mullite above 1075°C is as follows,

$$0.282Al_8\,(Al_{13.33}{}^*{}_{2.66})\,O_{32} \xrightarrow{\sim 1075^oC} 3Al_2O_3.2SiO_2 + 4SiO_2$$

or

$$0.562Si_8\,(Al_{10.67}{}^*{}_{5.33})\,O_{32} \xrightarrow{\sim 1075^oC} 3Al_2O_3.2SiO_2 + 4SiO_2$$

(7) At 1100- 1200°C the spinel is lost, elongated mullite crystals of up to 0.5µm length starts to develop. By reaching about 1300°C the melt gets saturated with quartz silica dissolution ends and hence the quartz to cristobalite transformation begins [1, 10].

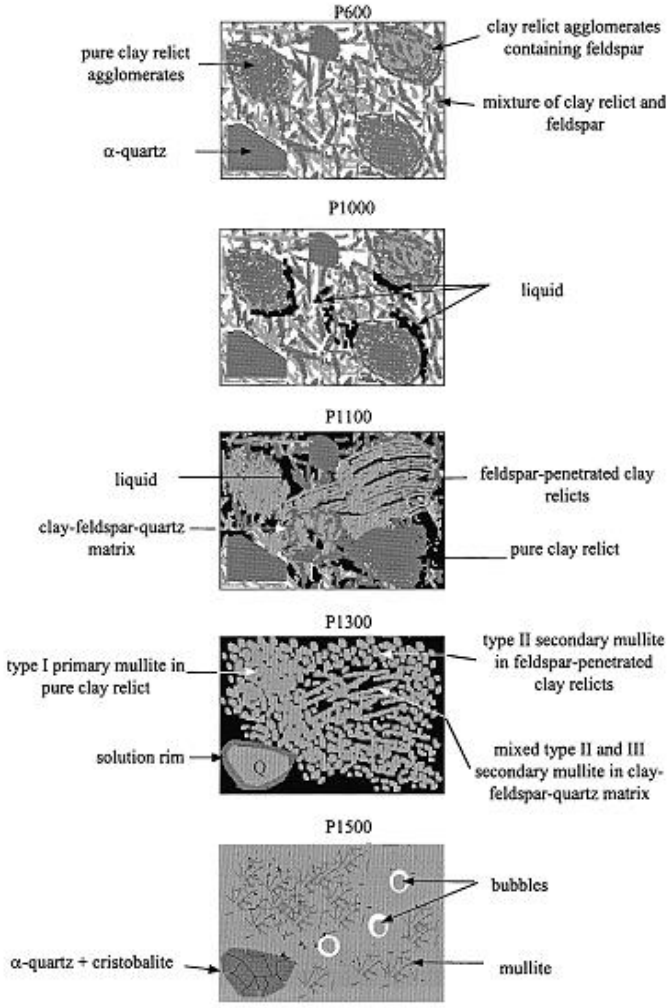
(8) Above temperature 1200°C the mullite crystals starts to grow as prismatic crystals, into the feldspar grain remaining's. At this temperature cristobalite and mullite are the only crystalline phases that remain in the body. Further increase in temperature above 1500°C cristobalite changes to amorphous glass [1, 11, 4-10].

The microstructure of porcelain bodies contains about 12- 25% mullite(may be $3Al_2O_3.2SiO_2$ or $2Al_2O_3.1SiO_2$), 5- 25% α- quartz and 0- 8% pores dispersed in 65- 80% potassium aluminosilicate glass [4, 5, 9].

Most of the researchers have found out 3 kinds of mullite species in porcelain. Among these three first one is the primary mullite which is short, having a scaly or flaky structure and is formed form the clay relicts. Next is the secondary mullite which formed by the reaction between feldspar and clay relicts at around 1200°C. The secondary mullite is also of two types, type-II and type-III which differ from each other because of its structure. The type-II mullite is short and have a granular morphology. Type-III mullite is of acicular structure and is highly elongated. They found that secondary mullite with interlocked structure and acicular morphology, having small needle diameters improves the mechanical properties of porcelain [1, 4, 10, 11]

Kausik Dana et al. [8] found out that at 1300°C a large amount of long secondary mullite (>1μm) with small primary mullite (< 1μm) cluster was found, the presence of these small primary mullite is due to the high viscosity of the silica rich glass. With increasing temperature secondary mullite and quartz dissolves in the glass melt, only primary mullite remain stable. At 1300°C porcelain body only contains mullite, quartz and glass, after 1350°C the quartz grains dissolves almost completely. They finalized that at 1300°C both the normal porcelain batch and fly ash batch was having similar microstructure, contained small primary mullite (< 1μm) and secondary mullite elongated (>1μm) found embedded within the glassy matrix.

Yaseen Iqbal et al. [4] explained that they found mullite at 1100°C and its amount was found increasing with the temperature increase and reached a maximum at 1400°C. They found small mullite (≤ 7nm) and ɤ- Al_2O_3 crystals precipitated from pure clay relicts and larger mullite crystals (≤ 30nm) in mixed clay- feldspar relicts at 1000°C. They found out the different mullites formed with respect to different regions. Regions with pure clay relicts was containing primary and scaly type- I mullite; regions with feldspar penetrated clay relict contained secondary mullite, granular type- II; and the matrix of quartz, clay and feldspar was having secondary type- II and secondary type- III mullites. Also TEM images showed cuboidal type-I mullite (≤ 0.1μm) in glassy matrix which formed from pure clay particles and feldspar penetrated granular microstructure having cuboidal (≤0.1μm) and longer (≤1μm) type-II mullite crystals. When fired at 1400°C bubbles was found forming in the microstructure at the region of clay relicts. In 1500°C fired batch long needle mullite (>10μm) in potassium silicate glass region and cracking of quartz grains was found which is a result of cristobalite transformation. The stages of microstructure formation in porcelain is given below in figure 2.2.1



Figure; 2.2.1 Stages of microstructure evolution in porcelain [4]

W. E Lee et al, [10] in their work on mullite formation in clays and clay derived vitreous ceramics explains that the mullite formation in vitreous ceramics is mainly from the clay and its reaction with other components. Also the acicular morphology, interlocking and the generated stress in the matrix affects the mechanical properties.

When porcelain was prepared from Algerian raw materials with a composition of 37wt% kaolin, 28wt% quartz and 35wt% feldspar higher density- 2.5g/cm3 was observed when fired at 1200^{o}C. They found that good mechanical properties and densification was obtained for the

uncalcined batch than the calcined batch. A very high flexural strength values of about 197 MPa was obtained which was about more than double values obtained for conventional porcelain (60-80MPa). Also very high Vickers hardness values of 9.1 to 9.3GPa was obtained [21].

C. Y. Chen et al. [5] shown that the mullite formation reaction is strongly dependent on precursor mixing. Mullitization by solid state reaction with Al_2O_3 and SiO_2 particle can be high as 1650^{o}C, by coating SiO_2 on γ-Al_2O_3 particle mullite formation occur at 1300^{o}C. On using sol- gel technique with atomic level mixing of Al, Si and O can lower the temperature to around 1150^{o}C. They have analyzed the shrinkage, found that first shrinkage was at around 500^{o}C due to removal of hydroxyl group. Next the formation of γ-Al_2O_3 or the spinel crystal cause shrinkage, followed by a considerable shrinkage above 1100^{o}C because of the first mullite grain formation. During their study only mullite phase was found for compact sintered at 1600^{o}C for 1 hour. Also the aspect ratio was found increasing with the increase in firing temperature.

2.3 Effect of Additives on Fired Properties of Tri-axial systems

G.N. Maslennikova et al. [14] in their review explained that there are normally four classes of additives that are used for porcelain preparation. Among those the first type include additives that controls the coagulation thixotropic structure of the porcelain suspension. It also controls its transition to condensation structure. The second type include additives which enhances the sintering process and helps the transformation from condensation structure to crystallization and crystallization pseudo coagulation structure. Third type include additives which enhances the crystallization of new forms. And the fourth category include additives which acts as source for crystalline phase formation and improving properties of porcelain such as light scattering action.

Most of the researchers found out that the mullite structure present in alumina silica binary system is able to incorporate a very large amount of transition metal oxides. The transition metal ions sometimes get into the Al_2O_4 terahedra or otherwise get incorporated with the AlO_6 octahedra of the mullite running parallel to the *c*-axis by replacing the Al^{3+}, or by getting into the voids generated by the oxygen removal from the octahedral positions. One another possible case was that the ions having larger size and lower valence cannot enter into these sites but they react with the ɤ-Al_2O_3 at lower temperatures (500- 1000^oC) and forms a defective metal alumina spinel structure ($MeAl_2O_4$).Among all the transition metals Cr^{3+}, V^{3+} and Fe^{3+} have the highest tendency for mullite incorporation, while Fe^{2+}, Co^{2+} and Mn^{2+} are least incorporated. The cobalt incorporated mullite was having formula, Co_yAl_{4+2x}-2_yO_{10-x}. They found that cobalt can be incorporated in both mullite and glassy phase [17, 22]. Most of these incorporations result in structural deformations or distortions. The transition metal cations include Ti^{3+}, Ti^{4+}, V^{3+}, V^{4+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Mn^{2+}, Cu^{2+}, Cu^{1+}, Ga^{3+}, Ni^{2+} etc. [7, 12, 13, 15-20, 22].

In the study ‘Effect of TiO_2 on the mullite formation and mechanical properties of alumina porcelain’, Noemi Montoya and his co-workers found that from the added TiO_2 additive, Ti^{4+} mullite solid solution was formed by the entering of Ti^{4+} into the secondary mullite structure. The mineralizer TiO_2 addition cause decrease in melt viscosity at the contact areas between TiO_2, clay relicts and feldspar grains. The viscosity decrease favors secondary mullite nucleation, as a result of this nucleation and the lower viscosity of feldspar melt, large secondary type-II and type-III mullites are formed. The formed primary mullite was shorter than 250nm, secondary mullites type-II and type-III were longer than 7.5µm, and also type-III mullite were thicker than 0.8µm.with TiO_2 addition increase in both bulk density and flexural strength was observed [11].

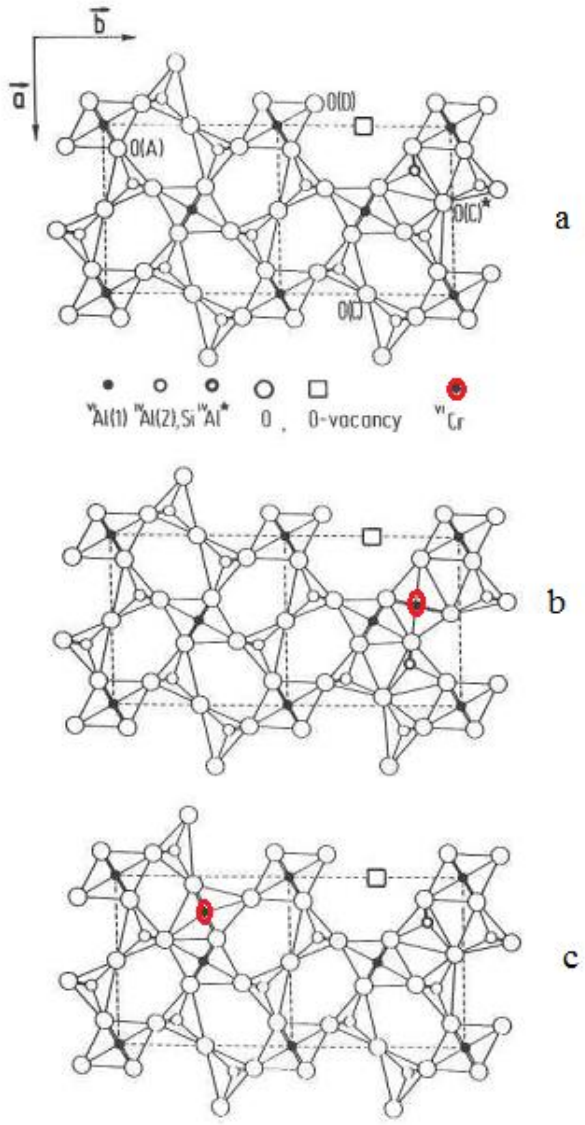
Sunipa Bhattacharyya et al. [6, 7] found with TiO_2 addition more glassy phase was forming, with quartz dissolution and also the mullite content was increasing with increase in TiO_2 content. Factors affecting shrinkage and expansion of samples were the formation of glassy phase, followed by the dissolution and reprecipitation of the crystalline phases. Because of the advance in reaction rates more liquid phase was obtained, hence lead to bloating large shrinkage values. A maximum of 45 MPa strength was obtained for the additive containing batches. After secondary recrystallization by controlled reheat treatment enhancement of strength up to 60 MPa and thermal shock resistance was observed.

Jagannath Roy et al. [13] in their work explained that different transition metal oxides work as favorable mineralizing agents in mullite formation. They have discussed that Manganese, copper oxide, V_2O_5, Nb_2O_5, Ta_2O_5, TiO_2 and Cr_2O_3 effects positively in the mullite formation. Most of them helps in reducing the temperature of conversion of kaolinite into mullite. During the firing by reaching a temperature of about 1050ºC the Cu_2O decomposes to Cu^{2+} (radius 87pm) and Cu^{1+} (radius 91pm). These ions substitutes Al^{3+} (radius 53pm) creates lattice expansion. The CuO improved the aluminum oxide solubility in silica matrix and also deform the SiO_4 tetrahedron layer and improve its reactivity with Al_2O_3.

$$Cu_2O + Al_2O_3 \rightarrow 2[Cu''_{Al}] + O_O^{xx} + 2V_O^{\cdot}$$

$$CuO + Al_2O_3 \rightarrow Cu'_{Al} + Al_{Al}^{xx} + O_O^{xx} + 0.5V_O^{\cdot}$$

The Al^{3+} substitution by Cu^{1+} and Cu^{2+} create anion vacancy at oxygen lattice and hence increases the rate of mullitization. Also the mechanical properties together with bulk density was found increasing.



Figure; 2.2.2 Models of Cr^{3+} incorporation into mullite, (a) Mullite without Cr, (b) Cr^{3+} substitution of $Al(1)^{3+}$ near the O vacancy, (c) Cr3+ substitution of $Al(2)^{3+}$ in the structural channels parallel to c-axis.[16]

N .K Mitra et al. [15] found out that $Cr^{3+}$is stable in mullite structure up to about 12 wt% of Cr_2O_3. At lower contents Cr^{3+}substitutes Al in octahedral position, but Cr^{3+}incorporation at the interstitial lattice sites were found for higher contents. For the incorporation of Cr^{3+} in the interstitial lattice Al^{3+} removal from the octahedral or tetrahedral was required to compensate the charge. This Cr^{3+} incorporation created a large expansion along *c*-axis together with expansion

along both *a* and *c*-axis of mullite. Their objective was to study the effect of Cr_2O_3 additive on mullitization and to eliminate the liquid phase during sintering and they found the true density, bulk density and shrinkage were increasing with the increase in Cr_2O_3 mineralizer content and temperature.

Some researchers found that the very low thermal expansion of mullite can be further decreased by its doping with chromium oxide. Also found that Cr^{3+} incorporation in octahedral position of AlO_6 is preferred when the Cr_2O_3 content is low and incorporation in interstitial lattice positions when Cr_2O_3 content is high. Because of chromium addition, in case of mullite derived from alumina silica gel 7% more mullite was formed with 3% additive introduction. Reduction in apparent porosity of about 30%, density increase of about 14%, 16% improvement in flexural strength and 6% improvement in fracture toughness was also obtained [18].

In the study on the effect of transition metal oxides on mullite whisker formation from mechano chemically activated powders, the researchers studied mullite formation in presence of CoO, $FeO_{1.5}$ and NiO in alumina silica binary system. They found that FeO addition enhances mullite formation while NiO and CoO inhibited mullitization at lower temperatures. The anisotropic mullite growth was enhanced by the addition of B_2O_3, TiO_2 and Fe_2O_3. In case of FeO addition mullite was observed even in the 1000^oC fired batch, while in other additive batches no mullite in this temperature. The order of transition metal oxides on the positive effect of mullite formation was FeO1.5 > CoO >NiO [20].

Debasis Roy et al. [24] worked on incorporating copper, nickel and cobalt in mullite and they found with increasing additive concentration mullite content was increasing on temperature moving from 1000^oC to 1300^oC. Also the mullite structure was changed from needle shape to plate

acicular shape and increase in densification observed. Enhanced mullite formation was observed only up to a certain amount of additive, after that it was found declining. Because the other alumina ions (Al^{3+}) were used for forming other phases of alumina such as metal aluminates and aluminum oxides. The dielectric properties were also studied, in which nickel oxide additive batch given good dielectric properties.

Kaimin Shih et al. [33] explained the formation of $NiAl_2O_4$ spinel and mullite formation from the mixing of kaolin and NiO. They found that mixing procedures, time and firing temperatures has a very large role in defining the phase formation and properties. Also the ball milled samples in presence of liquid phase given highest transformation ratios (more than 90%) in case of kaolin plus NiO mixture and also in the ɤ-alumina and NiO mixture. After firing above 1300ºC the batch was composed of mullite, $NiAl_2O_4$ and cristobalite. The nickel containing gamma alumina gradually gets converted into nickel aluminate spinel, by replacing the Al^{3+} with Ni^{2+}. But alumina silica spinel by around 1200oC transformed into mullite [28].

S. P. Chaudhuri et al. [25] prepared porcelain with Fe_2O_3, Cr_2O_3 and TiO_2 and studied characteristics before and after heat treatment. They found that the maximum amount of mullite that was present in porcelain batch was about 39.9 wt%. With the aid of heat treatment at 1150ºC for 50 hours the mullite percent was found increasing to about 42.6 wt%. Nb_2O_5 and V_2O_5 acted as efficient mullitization agents. TiO_2 retards mullitization at higher concentrations, whereas at lower concentrations act as a nucleating agent provides an extra liquid phase which helps in mullite formation. Also about 10-30 wt% alumina and glassy phase was present in batch before heat treatment. This alumina and glass undergone nucleation and crystallizion which created an extra 6-7wt% mullite during heat treatment. But Cr_2O_3 because of its refractory nature did not produced any liquid phase. Heat treatment of Cr_2O_3 containing batches marginally increased the mullite size

but the other additive batches helped in growing larger mullite crystals, whereas TiO_2 acted as a very good mineralizer in enhancing the large acicular mullite formation [26].

J. Roy et al. [27] showed that the morphology of mullite crystal has developed with cobalt addition, maximum expansion was along *b*-axis. About 14% extra mullite formation was observed with 3% CoO addition. In the presence of CoO, cobalt aluminate spinel and cobalt silicate was found forming which finally lead to mullite formation where CoO reduces the energy barrier for mullite formation, reactions are given below.

$$3(Al_2O_3.SiO_2) + 2CoSiO_4 \rightarrow 2CoO + 3Al_2O_3.2SiO_2 + 3SiO_2$$

$$2(Al_2O_3.SiO_2) + 3CoAl_2O_4 \rightarrow 3CoO + 3Al_2O_3.2SiO_2 + 2Al_2O_3$$

Reduction in porosity, about 10% increase in bulk density and also flexural strength development of about 5% was observed.

CHAPTER- III

EXPERIMENTAL WORK

3.1. Raw materials

The commercially available raw materials of Indian origin were used for the study. They include the basic tri-axial composition like china clay, ball clay, quartz, feldspar and the transition metal oxide additives such as Chromium Oxide (Cr_2O_3), Cobalt Oxide (CoO) and Nickel Oxide (NiO). During the compaction 3% polyvinyl alcohol was used as the binder. The chemical analysis of the raw materials were done and is given below;

Chemical constituents (wt%)	China clay	Ball clay	Quartz	Feldspar
SiO_2	49.28	57.55	98.65	65.23
Al_2O_3	32.95	30.23	0.39	18.31
Fe_2O_3	0.58	1.23	0.07	0.12
CaO	1.88	0.44	0.10	0.43
MgO	0.59	0.31	Trace	Trace
Na_2O	0.72	0.28	0.09	2.94
K_2O	0.45	0.81	0.12	11.32
L.O.I	13.4	9.12	0.39	0.87

Table; 3.1 Chemical analysis data of the raw materials

3.2. Batch preparation

For the study a total of nine different batches were prepared among them one batch was of pure tri-axial composition, two batches with Cr2O3 additive, three with NiO additive and last three batches with CoO additive, the batch composition is given below.

A total of 100gm of each batch were prepared following the given composition -

Batch	**China Clay (gm)**	**Ball Clay (gm)**	**Quartz (gm)**	**Feldspar(gm)**	**Cr_2O_3 (gm)**
Batch- 1	40	10	25	25	0
Batch- 2	39.2	9.8	24.5	24.5	2
Batch- 3	38.4	9.6	24	24	4
Batch	**China Clay (gm)**	**Ball Clay (gm)**	**Quartz(gm)**	**Feldspar(gm)**	**NiO(gm)**
Batch- 4	39.6	9.9	24.75	24.75	1
Batch- 5	38.8	9.7	24.25	24.25	3
Batch- 6	38	9.5	23.75	23.75	5
Batch	**China Clay (gm)**	**Ball Clay (gm)**	**Quartz(gm)**	**Feldspar(gm)**	**Co_3O_4(gm)**
Batch- 7	39.6	9.9	24.75	24.75	1
Batch- 8	38.8	9.7	24.25	24.25	3
Batch- 9	38	9.5	23.75	23.75	5

Table; 3.2 Batch composition of raw materials

3.3. Mixing

The powders were weighed according to the composition given in table-2 and mixed together as separate batches. The batches were taken in separate plastic containers, added with equal amount of distilled water, closed tight and kept for pot milling. Milling was done continuously for five hours and alumina balls were used as the grinding medium. After the milling was complete, prepared slurry was poured out and kept for drying in a petri dish initially at 40^{o}C then at around 120°C for more than 10 hours. This drying causes most of the water present in the slurry to be escaped and it gets into a solid form. This dried up slurry was ground to fine powders with an agate mortar.

3.4. Calcination

The fine powder obtained after grinding the dried up slurry was kept for calcination to remove the molecular water present in the clay structures which cannot be relieved by low temperature drying. So the powders were kept in the furnace in alumina crucibles and fired at 900°C for 2 hours, at a rate of 10°C/ min and was cooled down normally. Due to the calcination at this temperature most of the water present escapes and nucleation initiated.

3.5. Fabrication of Compact Mass

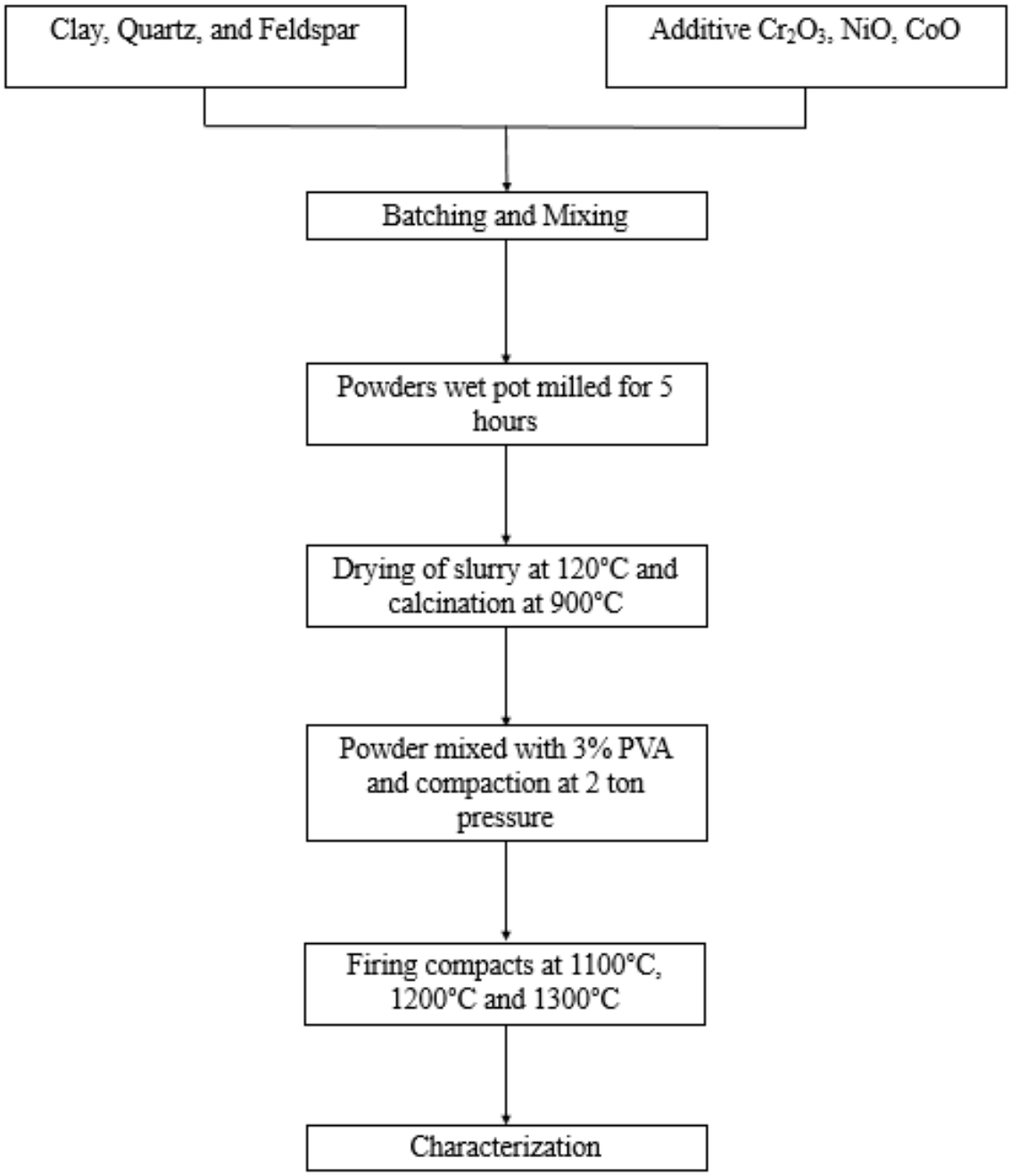
The calcined powder was mixed with 3% Poly Vinyl Alcohol solution which is the binder that provides the bonding strength and the dimensional rigidity for the green compact. The powder was mixed well with the binder, dried in light and pressed uniaxially using a hydraulic press and prepared bars of dimension 15mm x 5mm and 50mm x 5mm. Compaction was done at a pressure of 2 ton for a holding time of 90 seconds. Sixteen pellets of each batch were prepared. During the pressing steric acid was used as lubricant and acetone to clean the die.

3.6. Sintering of the fabricated bars

Each batch were then sintered in an electrically operated laboratory furnace at three different temperatures, 1100°C, 1200°C and 1300°C having four pellets in each. The firing schedule was in such a manner that,

- Heating rate was 4°C/min at the starting, fired up to 500°C and kept there for 60 minutes soaking so that the binder gets burnt out.
- After soaking, again heated with a rate of 7°C/min up to the required maximum temperature and followed by 90 minutes soaking.
- Then cooled down normally to atmospheric temperature.

A flow chart of the whole process is given below,



Figure; 3.1 Flow chart of the whole processes

3.7. Characterization and measurement techniques used;

The characterization techniques used to find out the physico-mechanical properties such as bulk density, percent apparent porosity, percentage linear shrinkage, flexural strength etc. of the compacts were performed. For finding out bulk density and apparent porosity Archimedes method was used. The length, breadth height and weight of the green and the sintered compacts were measured. For performing the Archimedes method, the sintered compacts were kept in boiling water for two hours. Due to this continuous boiling the air bubbles present even in the minute pores of the sintered compact gets escaped and water enters into it. After the boiling was completed, the weight of bars was measured at suspended condition which was recorded as suspended weight. The excess water from the compact surface was wiped off with a cotton cloth and the soaked weight was measured. The calculations were performed with respect to the collected data.

3.7(a) Green Density-

Green densityis the ratio of mass of the green body to its volume.

Green density= mass / volume (gm/cm^2)

3.7(b) Percentage Linear Shrinkage-

The change in dimension with temperature is measured as shrinkage or expansion. But ceramic generally shows shrinkage not expansion. So the linear or volumetric shrinkage is measured. Linear shrinkage is percentage change in the linear dimension of the fired sample with respect to unfired. The dimensions of the unfired body are measured and then the dimensions of

fired are measured. Then by subtracting final length from the initial length we get the linear shrinkage. To get the percentage linear shrinkage value we use the following formula:

Percentage Linear Shrinkage= $\frac{L_1-L_2}{L_1}$ x 100

Where, L_1= length of green body, L_2= length of the sintered body.

3.7(c) Bulk Density-

It is the ratio between the mass of material of a porous body and its bulk volume.

Bulk density= Dry weight /Soaked weight- Suspended weight × ρ g/cm3

Where $\boldsymbol{\rho}$ is the density of the medium, here water was medium & its density is 1gm/cc.

3.7(d) Apparent Porosity-

Apparent porosity can be characterized by the volume fraction of pores (or voids) present. It is the percentage relationship between the volume of the pores space and the total volume of the sample. Water absorption is also measured with same experiment. Formulas used are:

Apparent porosity= (soaked weight- dry weight) / (soaked weight- suspended weight).

3.7(e) DTA Analysis-

The Differential Thermal Analysis was performed to find out the nature of the reactions and the mass change that was occurring during the firing stages of a body. The analysis was done up to 1000^{o}C at a rate of 10oC/min with the presence of nitrogen atmosphere.

3.7(f) Flexural Strength Test-

It is defined as the ability of a brittle material to resist undergoing deformation under load. It is also known as modulus of rupture, fracture strength or bend strength. Three point bend test is used to find out the flexural strength of a specimen, which may be circular or bar. The flexural strength value gives the maximum stress value that can be sustained by a material just before undergoing fracture. This test was performed using a universal testing machine, TINIUS OLSEN H10K-S UTM. In the case of a rectangular bar, flexural strength is given by the equation,

$$\sigma = \frac{F}{bd}$$

Where, σ= the maximum stress, *F*= the axial force applied, b= width and d= the thickness of the specimen. The unit of flexural strength is- MPa or N/m^2.

3.7(g) Phase Identification (XRD Analysis)-

X- Ray Diffraction study was done to find out the different phases of the materials present in the batches after firing at different temperatures. For this the samples were crushed and ground into fine powder and the study was done using copper Kα radiation. The data obtained was analyzed with the Philips X- Pert High Score software and the peaks were identified.

3.7(h) Microstructure Analysis (FESEM)-

Microstructure analysis was done using Field Emission Scanning Electron Microscope (Nova Nano SEM/ FEI 450). The images of the polished surface was taken. For obtaining good images of mullite the silica present in the sample was removed by HF etching. For etching 5% HF solution was prepared, the samples were kept in the solution for about 3-4 minutes and again

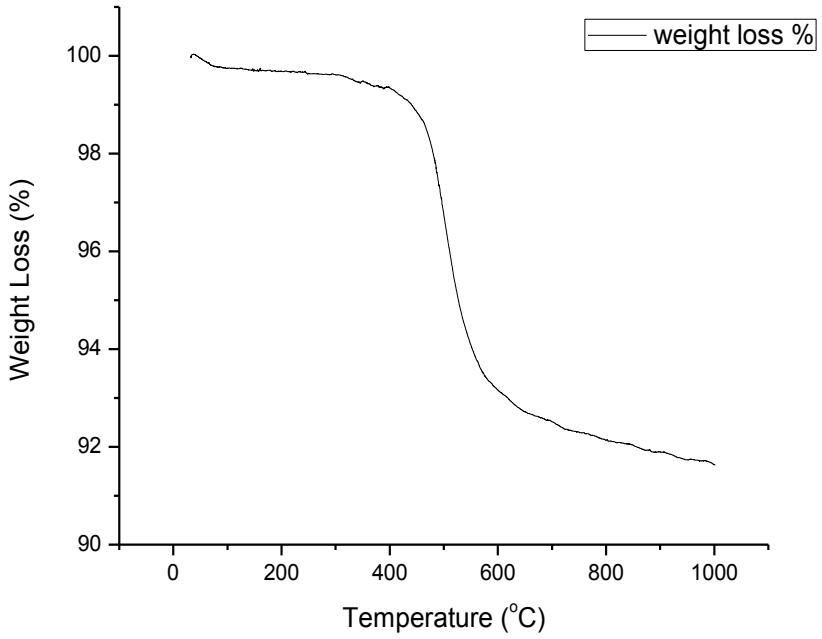
washed well with distilled water and acetone. Also platinum coating was applied on the samples to make the sample surface conducting.

CHAPTER- IV

RESULTS AND DISCUSSIONS

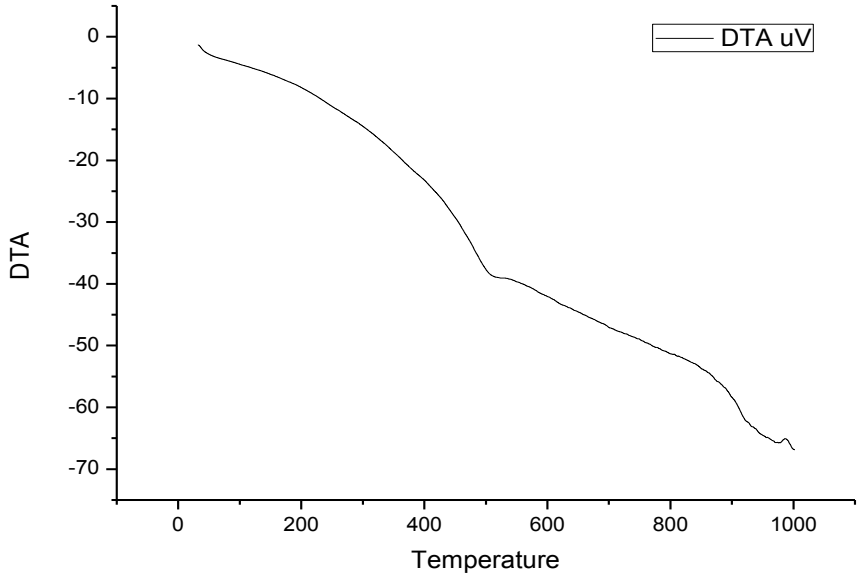
4.1 DTA Analysis of raw powder mixtures

For tri-axial ceramics reactions in the pre-sintering stages are very important, as they affect the properties and microstructure of final product. Depending on the physical and chemical changes occur during this pre-sintering stage firing schedule of the ceramic is designed. TG- DTA studies generally done for determining those physical and chemical changes during pre-sintering stages.



Figure; 4.1.1 (a) TGA analysis of pure clay, quartz, feldspar mixture.

Figure 4.2.1(a) and 4.2.1(b) are the TG and DTA curves for a typical porcelain composition in the absence of any additives. Here the TGA profile shows the total mass loss is around 8.3%. Since the tri-axial composition contains 50% clay, this mass loss is due to the decomposition of clay part.



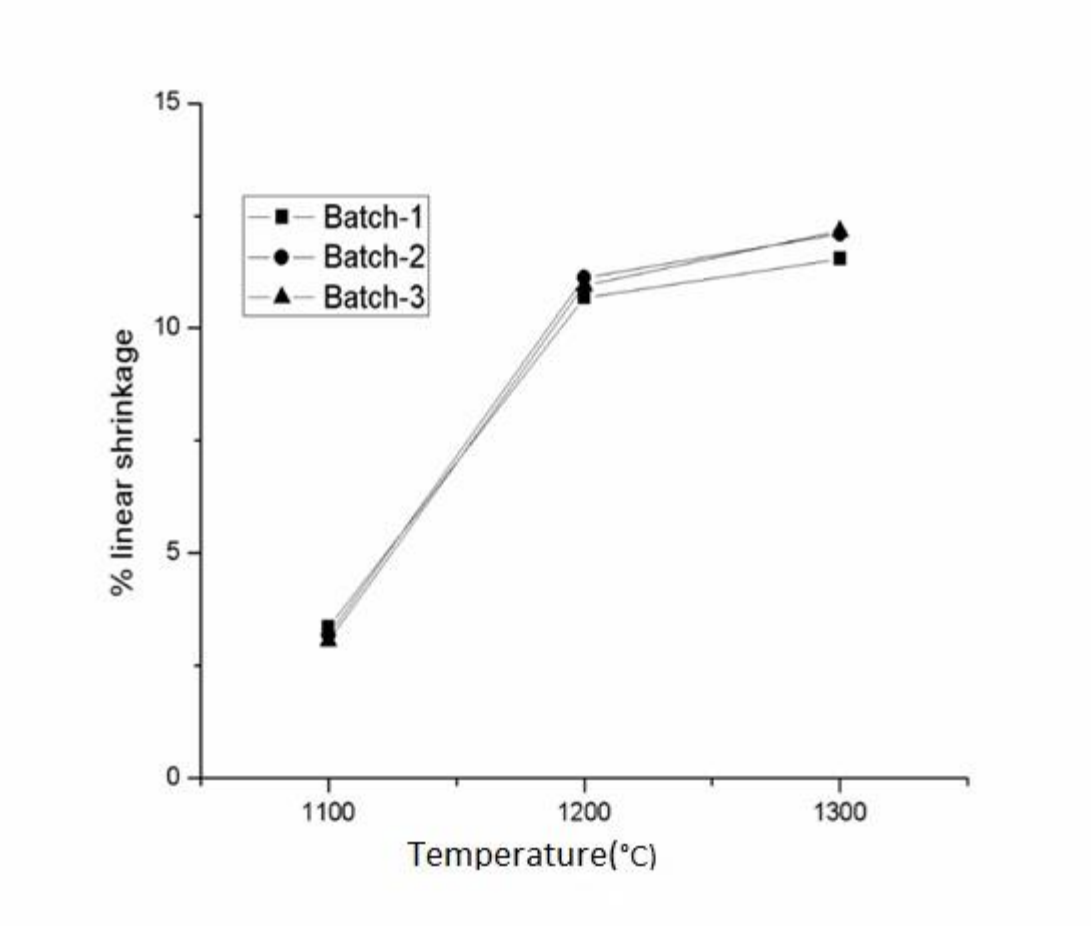
Figure; 4.1.1(b) DTA analysis of pure clay, quartz, feldspar mixture.

In fig. 4.2.1(b) the first endothermic peak at around 40^{o}C is due to dehydration, which is the loss of physically absorbed water [30, 31]. The second endothermic peak at around 500^{o}C is due to dehydroxylation of clay to form metakaolinite. The exotherm around 990^{o}C corresponds to the formation of alumina- silica spinel phase from the decomposition of metakaolinite. These two curves actually represent the nature of physical and chemical changes occurring due to pre-sintering of porcelain [30, 31].

CHAPTER- I

Effect of Cr_2O_3

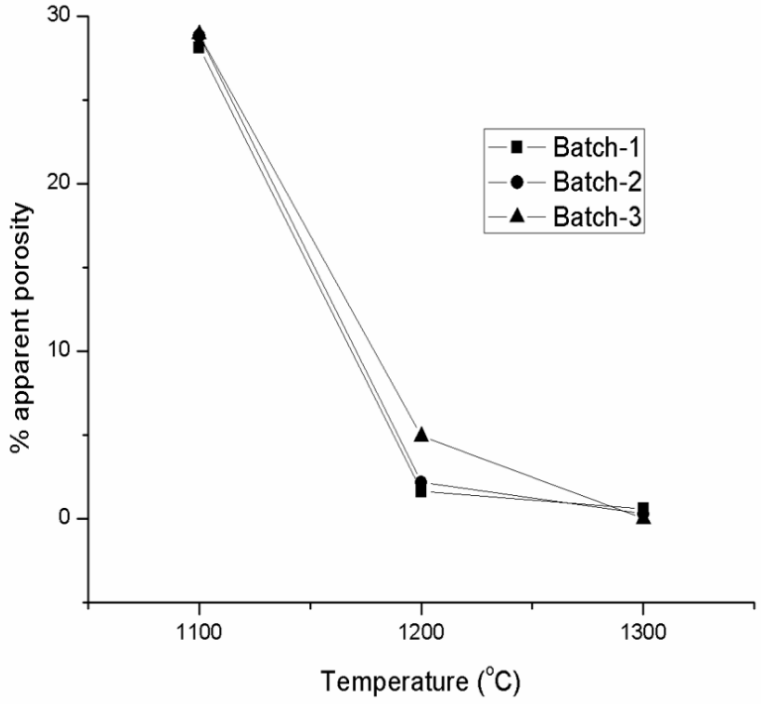
4.1 Effect of Chromium oxide



Figure; 4.1.1 Variation of Percent Linear shrinkage with temperature for Cr_2O_3 batch.

Figure 4.1.1 shows the variation of percent linear shrinkage with temperature. From the figure it was found that the shrinkage was increasing for all batches as the sintering temperature is rising from 1100^{o}C to 1300°C. This is due to more liquid phase formation and crystallization with rising temperature. Normally for porcelain batch mullite formation starts around 1100°C and glassy phase formation was continued, hence shrinkage rates observed to be increasing because of this crystallization reactions and liquid phase formation. Cr_2O_3 because of its refractory nature does not help liquid formation, so at lower temperature range at 1100^{o}C additive containing batch

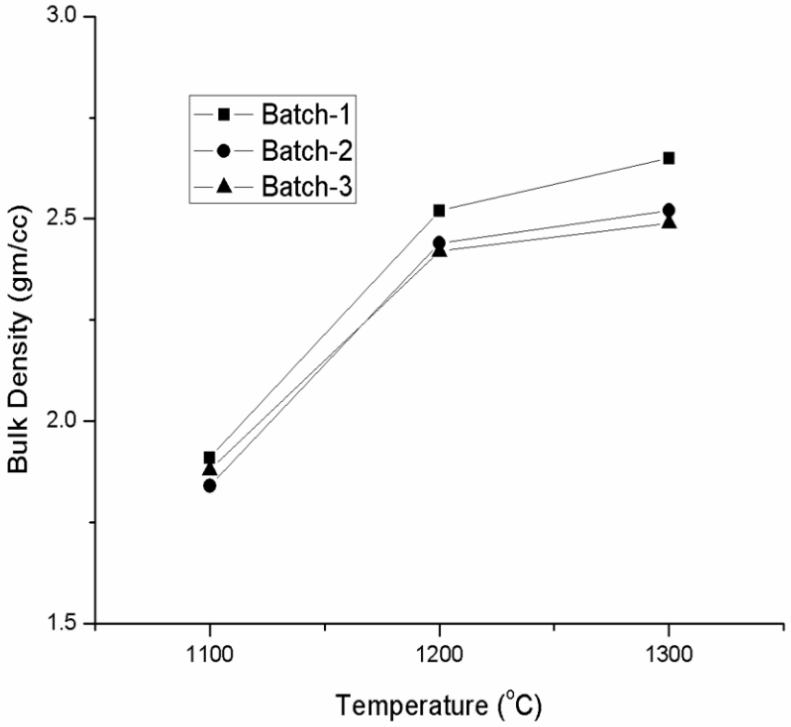
exhibit lesser shrinkage but at higher temperature at 1300°C it exhibit higher shrinkage due to delayed liquid formation [15].



Figure; 4.1.2 Variation of Percent Apparent porosity with temperature for Cr_2O_3 batch.

Figure 4.1.2 represents the variation of percent apparent porosity with temperature. From the graph it is evident that high reduction in porosity was found when porcelain samples of all batches were fired at 1200°C, which was due to the mass transport occurring as a result of glassy phase formation. The glassy phase formed enters into the pores present in the compact and fills the pores. Due to this, spherical pores are formed and also the compact gets densified. As we have explained earlier, Cr_2O_3 because of its refractory nature does not help liquid formation. So liquid formation in without additive batch is higher in low temperature zone for which without additive batch exhibit higher shrinkage and low porosity at low temperature zone, whereas at higher

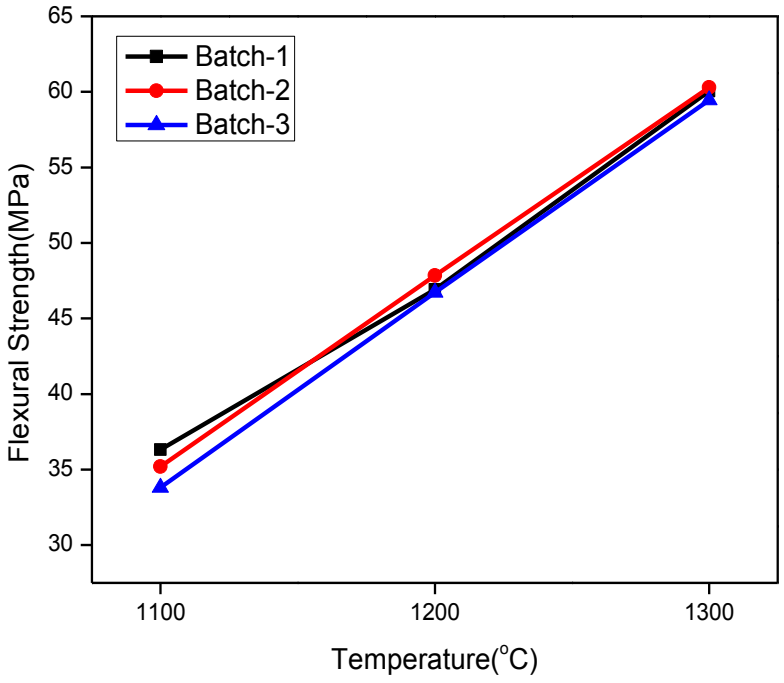
temperature 1300ºC due to the delayed liquid formation in additive containing batches they exhibit comparatively lesser amount of porosity. From 1200ºC to 1300ºC the change is sharp for 4% additive containing batch as here delayed liquid formation occurs. At 1300°C for 4% additive the porosity obtained was zero percent.



Figure; 4.1.3 Variation of Bulk density with temperature for Cr_2O_3 batch.

Figure 4.1.3 exhibits the variation of bulk density with temperature. The results observed proves the result for apparent porosity, i.e. the porosity decrease occur when the body becomes denser. For the whole batch the density increase was a little large on moving from temperature 1100°C to 1200°C. While moving on to the next temperature the curve was found somewhat linear. The glassy phase formation followed by viscous flow enhances the densification process caused the bulk density increase. At all the firing temperature without additive batch has the higher bulk

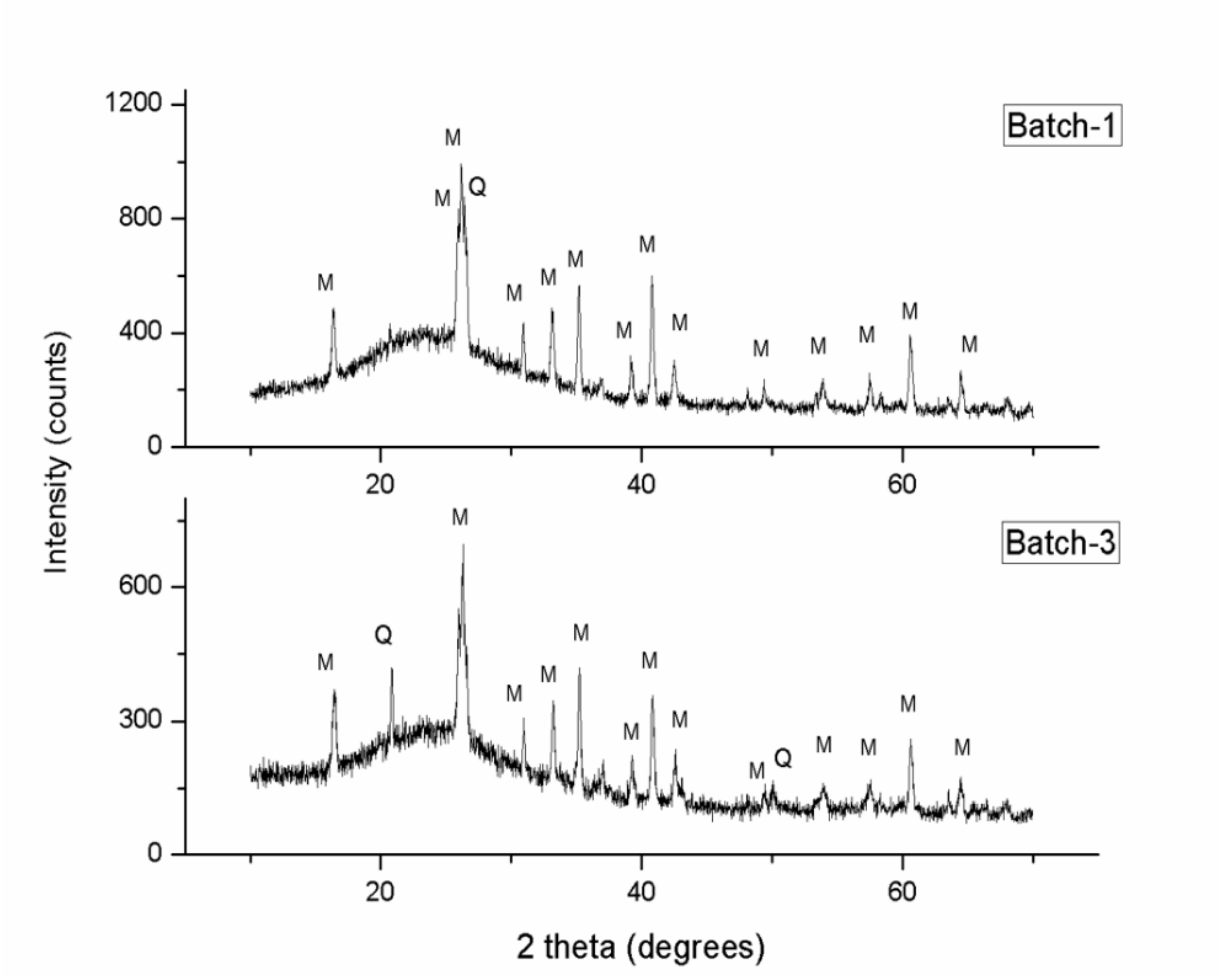
density followed by 2wt% and 4wt% additive content. As we told earlier the liquid phase formation is higher for without additive batch so the formation of mullite phase which is basically enhanced by the presence of liquid phase is more for without additive batch than additive containing batch. The bulk density is related with the final phases present in the system, as in case of without additive batch mullite crystallization is comparatively higher so the B.D values of without additive batch are always higher than additive containing batch. From XRD data it was found that mullite content decreases in presence of additive which supports this phenomenon.



Figure; 4.1.4 Variation of Flexural Strength with Temperature for Cr_2O_3 batch.

Figure 4.1.4 shows the variation of Flexural strength with temperature. From the graph we can see that there is no much variation in the case of flexural strength also because of chromium oxide addition. When the sample was fired at 1100°C, 4% Cr_2O_3 batch shown the least value for

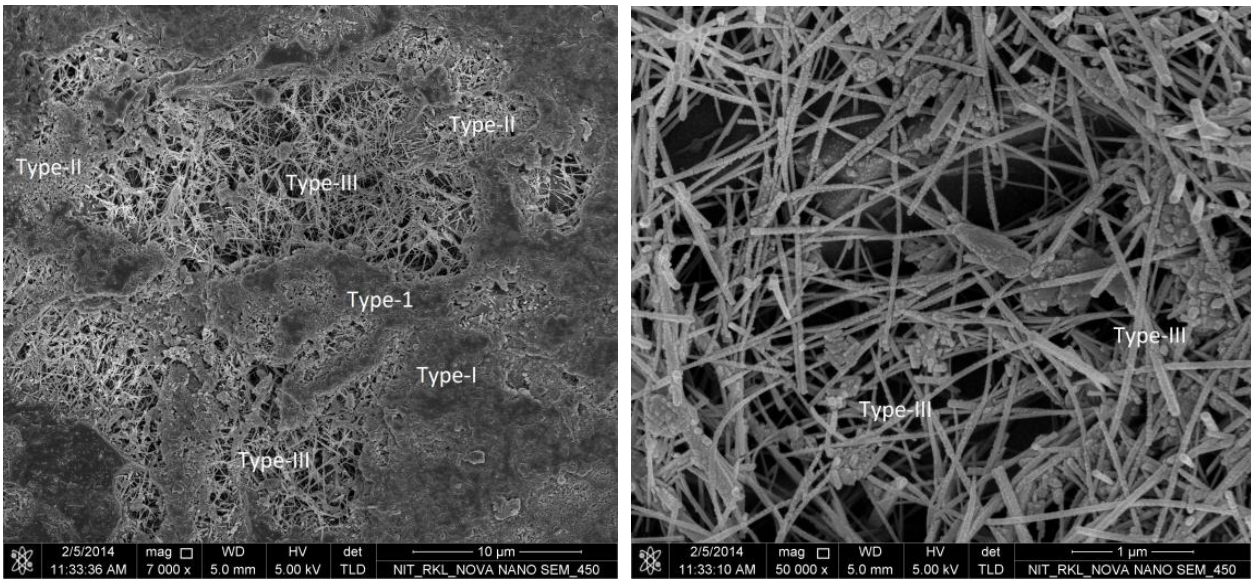
strength. Also moving on to the next temperatures and different additive percentages there is no appreciable variation in strength was found. Since mullite and glassy phase are the main constituents which determines the strength of a tri-axial composition, the result we found out becomes clearer. That chromium because of its refractory nature does not help in liquid phase formation and hence mullite formation. Figure given below shows the XRD analysis data of with and without additive batches fired at 1300^{o}C.



Figure; 4.1.5 XRD patterns of 1300oC fired without additive and 4% additive batch.

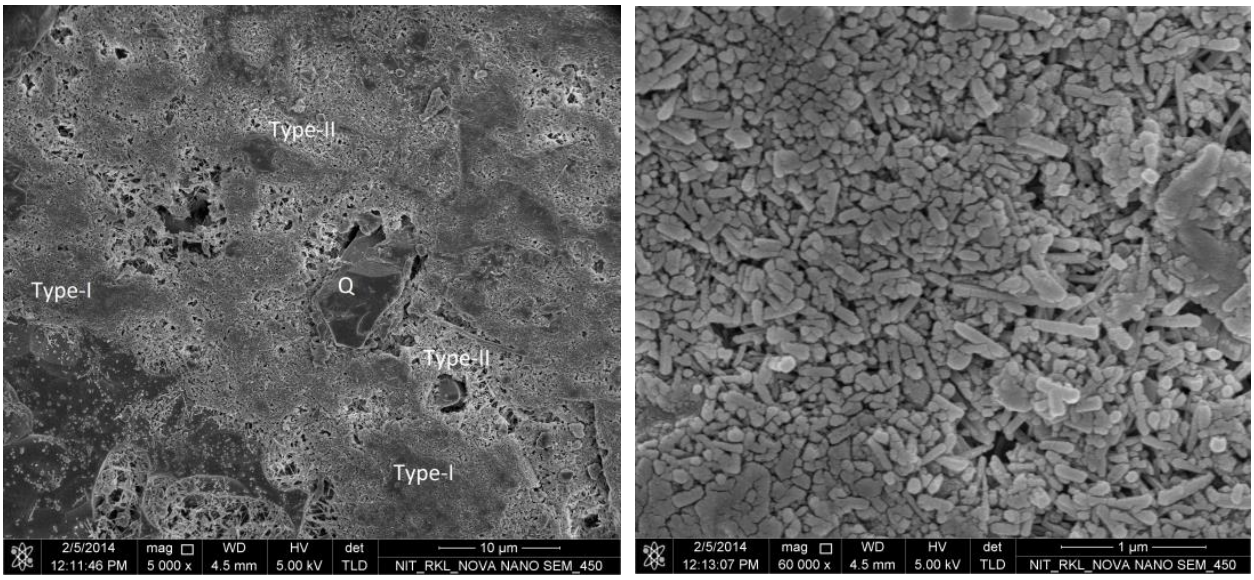
The XRD patterns of the samples with 4% Cr_2O_3 additive and without additive fired at 1300°C is represented in the figure 4.1.5. From the x-ray diffraction study performed it was found

that mullite and quartz are the major phases present in the body. Form the semi quantitative analysis it was found that mullite content decreases as percent additive increases. For without additive batch (batch-1) mullite content is 84% whereas for 4% additive containing batch (batch-3) mullite content is 68% (on the basis of semi quantitative analysis done by using X'pert High Score software). It clearly indicates presence of Cr_2O_3 hampers mullite formation. From heights of the peaks it is also evident that mullite content decrease with increase in Cr_2O_3 content. The role of mineralizer is to provide a liquid phase that assisted mullite formation by the dissolution precipitation mechanism but because of the refractory nature of Cr_2O_3 it failed to provide a liquid phase and there by the mullite content of the Cr_2O_3 containing batch dropped. The dissolution process of quartz is also slowed down by the presence of this additive. This drop of mullite content is also responsible for decrease in bulk density value in presence of 4% Cr_2O_3 at 1300^{o}C fired batches.



Figure; 4.1.6(a) and 4.1.6(b) FESEM images of 0% additive batch fired at 1300^{o}C.

Figure 4.1.6(a) shows primary type-I and secondary type-II mullite. Primary Type-I mullite are small scaly mullite derived from clay relict, those are formed at the surface of pure clay agglomerates. Needle shaped secondary type-II mullite crystals having aspect ratio nearly 5:1are found particularly in those regions where feldspar has penetrated clay agglomerates. The growth of mullite crystal through diffusion mechanism is favored in presence of liquid phase [32] as feldspar provides low viscosity glass in the penetrating zone so the formation of secondary type-II mullite favored in those zone. The presence of both type-I and type-II mullite were also found in fig. 4.1.6(a) and 4.1.6(b). In these figures there are some zones where greater longitudinal growth were still observed, here mullite needles having aspect ratio in the range of 30:1 were found and those are known as secondary type-III mullite. Type-III mullites were derived from the region containing homogeneous mixture of small size clay quartz and feldspar particle having lower viscosity. According to Iqbal and lee [17] these mullites are not Type-II or Type- III mullite, they suggested that these are cluster or packs of needles formed by the joining of mullite fibers having aspect ratio >30:1.The presence of Type II and type III mullite having high aspect ratio in the microstructure of without additive batch indicates the presence of higher amount of lower viscosity glassy phase in those samples.



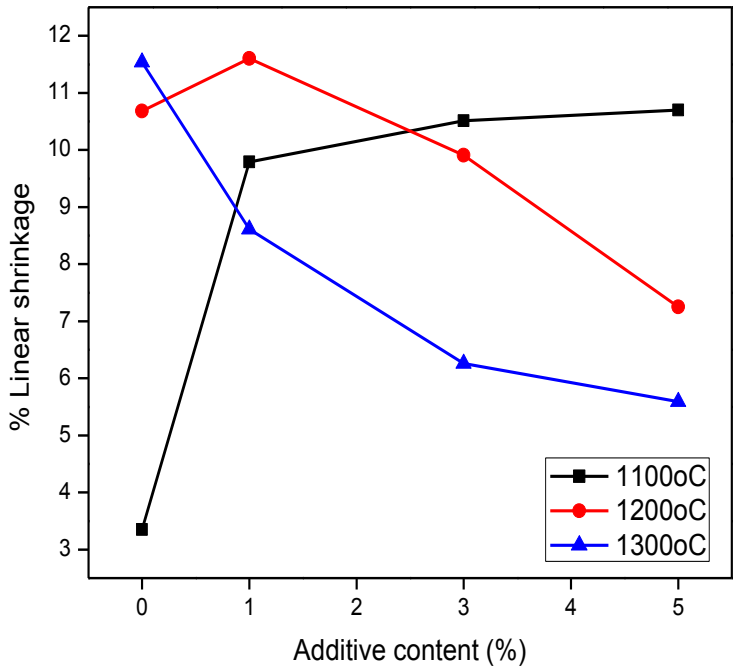
Figure; 4.1.7(a) and 4.1.7(b) FESEM images of 4% Cr_2O_3 batches fired at 1300°C.

Figure 4.1.7(a), 4.1.7(b) show the micrograph of 4% Cr_2O_3 additive containing batch. From Fig-4.1.7(a) it is found that along with residual quartz crystal primary mullite and secondary type-II mullites are present but one striking difference with the previous microstructures of without additive batch is that here the amount of secondary type-III mullite having high aspect ratio are very small. It is believed that secondary mullites are formed from the recrystallization and dissolution of aluminosilicate in melt, so the formation of secondary mullite with high aspect ratio is very much related with the formation of liquid phase. In microstructure if niddle shaped mullite is absent then it is due to the absence of sufficient amount of liquid phase. The efficiency of mineralizer depends on their fluxing action and on their solubulity in glassy phase of the sample. Here the refractory nature and low solubility of Cr_2O_3 appeared to be responsible for lesser amount of higher aspect ratio mullite in additive containing sample.

CHAPTER- II

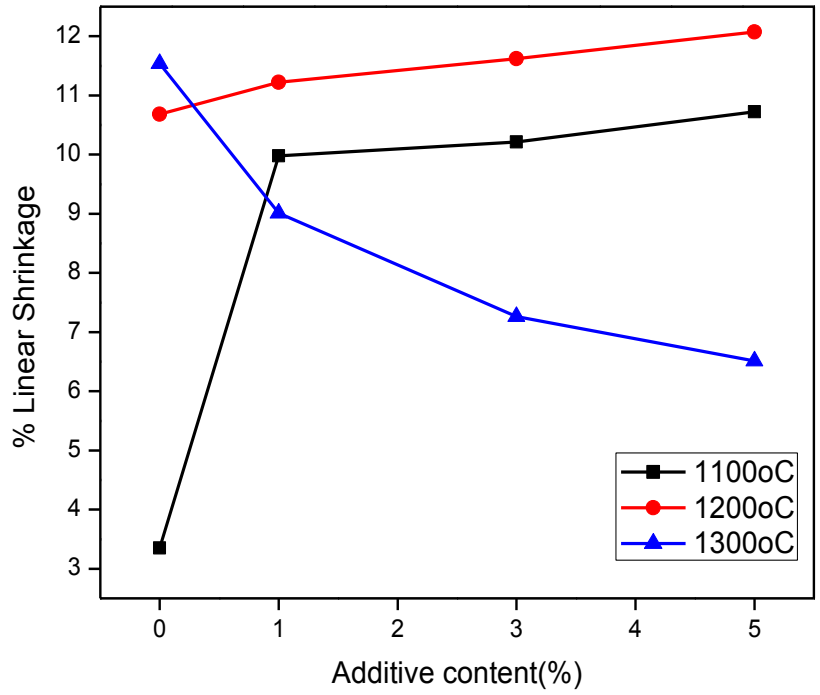
Effect of CoO and NiO

4.2 Effect of CoO and NiO



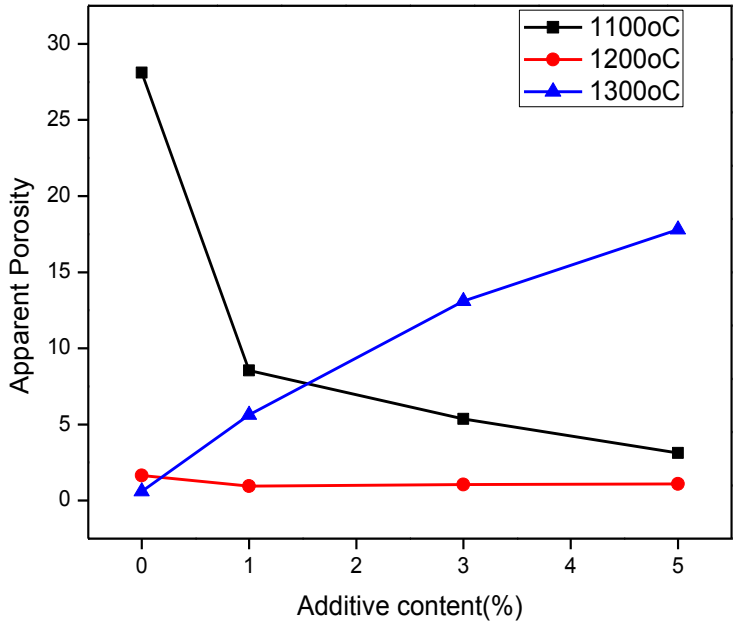
Figure; 4.2.2(a) Variation of Percent linear shrinkage with the amount of CoO additive added.

Figure 4.2.2(a) represents the variation of percent linear shrinkage with amount of cobalt oxide additive added at three different temperatures. From the figure it is clear that at 1100^{o}C when 1% CoO additive is added as a sintering aid thus percent linear shrinkage increase sharply. Then with further addition of additive, the nature of curve become flattened. At higher temperature 1200^{o}C compared to without additive batch the shrinkage increase only for 1% CoO batch, then decrease for higher percentage of CoO. At 1300^{o}C addition of CoO rather decrease the percent linear shrinkage value regularly. Here the maximum shrinkage was shown by 1% CoO containing batch at 1200^{o}C.

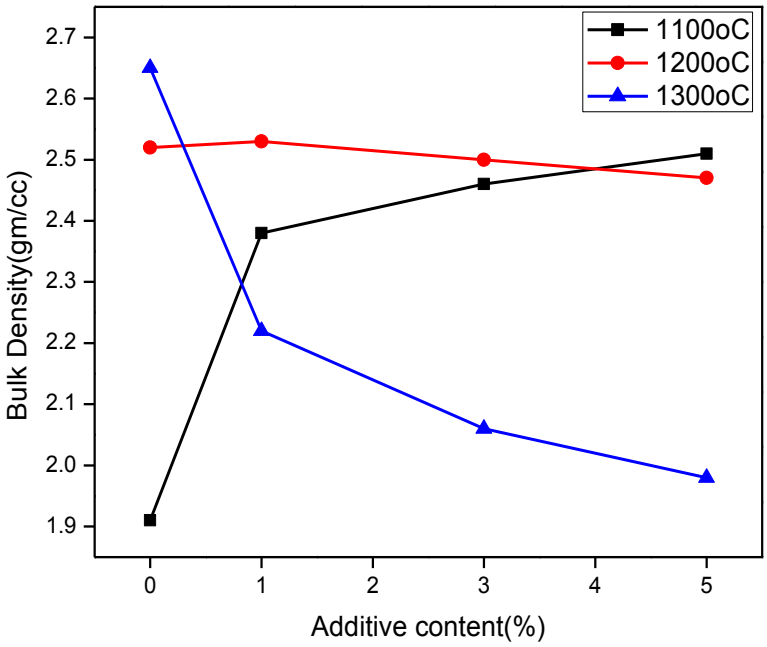


Figure; 4.2.2(b) Variation of Percent linear shrinkage with the amount of NiO additive added.

Figure 4.2.2(b) shows variation of percent linear shrinkage with amount of NiO additive added at three different temperatures. The nature of curve for 1100^{o}C and 1300^{o}C are similar to that of previous CoO batch. Only for 1200^{o}C fired samples a slight increase in trend with increase in additive content. Maximum shrinkage was shown by 5% NiO containing batch at 1200^{o}C.

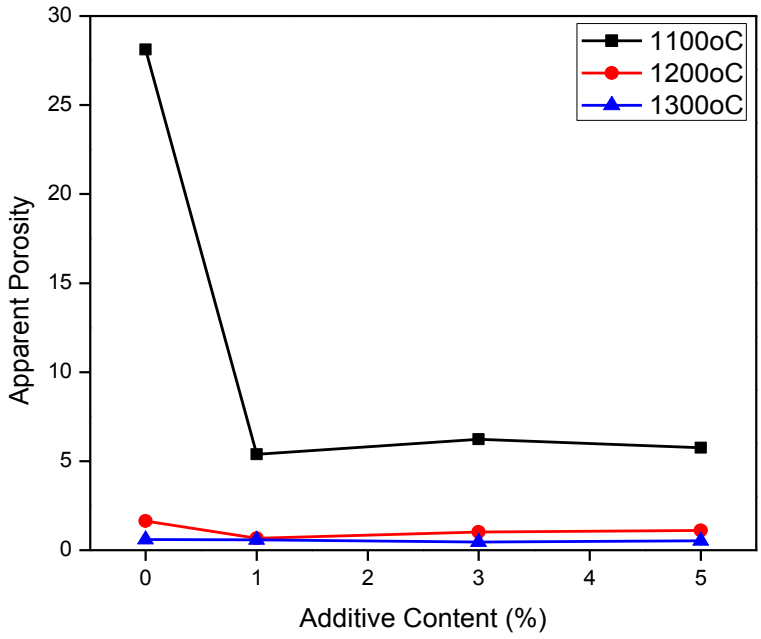


Figure; 4.2.3(a) Variation of Apparent porosity with the amount of CoO additive added.

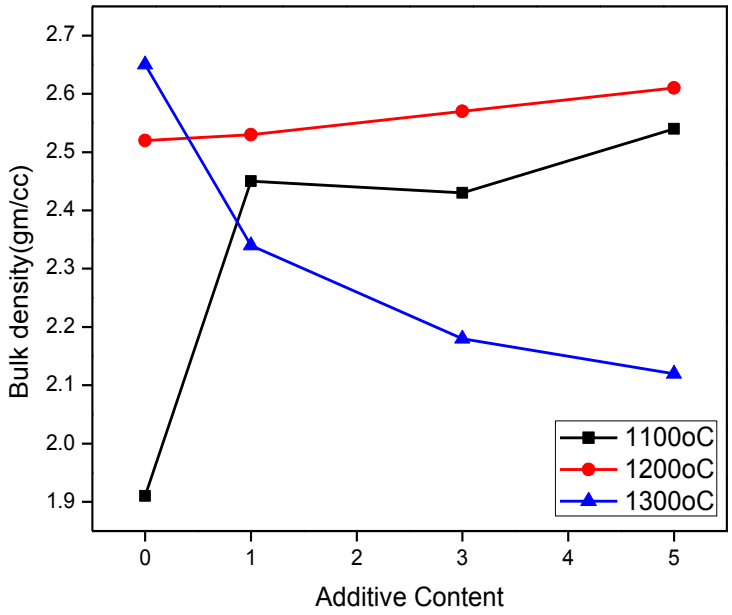


Figure; 4.2.3(b) Variation of Bulk density with the amount of CoO additive added.

Figure 4.2.3(a) and 4.2.3(b) showing variation of apparent porosity and bulk density with amount of CoO additive added at three different temperatures. From the curves we can see the property improvement due to additive incorporation can only be expressed with 1100^{o}C fired batches. But at higher temperatures for 1200^{o}C changes are not very prominent and 1300^{o}C instead of property modification, degradation of properties were observed.



Figure; 4.2.4(a) Variation of Apparent porosity with the amount of NiO additive added.

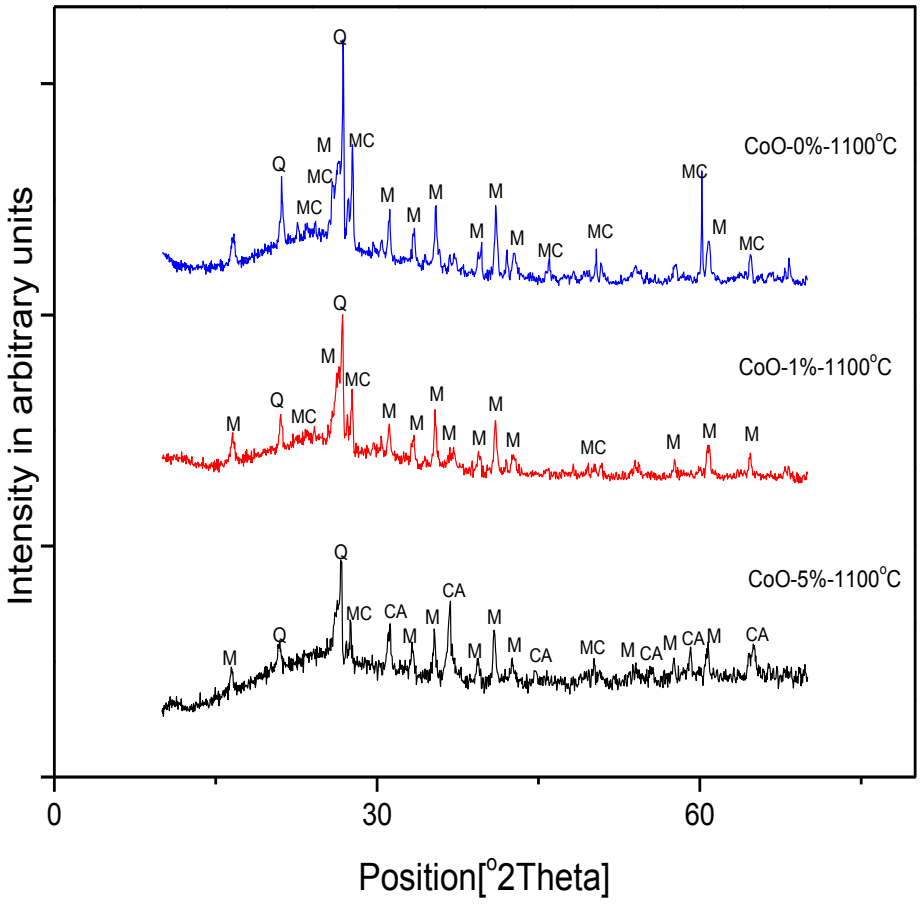


Figure; 4.2.4(b) Variation of Bulk density with the amount of NiO additive added.

Figure 4.2.4(a) and 4.2.4(b) represent the variation of apparent porosity and bulk density with the amount of additive added at three different temperatures. From fig.4.2.4(a) it is clear that at higher temperature range 1200^{o}C- 1300^{o}C presence of NiO is not beneficial as it does not help to reduce porosity or enhance bulk density. Only at 1200^{o}C for 5% additive batch bulk density value increased. But at 1100^{o}C remarkable changes are found with the addition of 1% NiO and with increase in additive amount the change in percent apparent porosity and bulk density values are not very much prominent. Actually the effect of CoO and NiO is related with the reduction in viscosity of silica rich glassy phase [19, 20].

In porcelain composition where clay, quartz and feldspar are present, in the absence of any additive, sintering process is initiated at around 950^{o}C by the process of thermal diffusion. And above 1000^{o}C primary mullite forms from clay along with silica rich glassy phase. NiO and CoO additives reduces the viscosity of that glassy phase and also help the dissolution of quartz. So

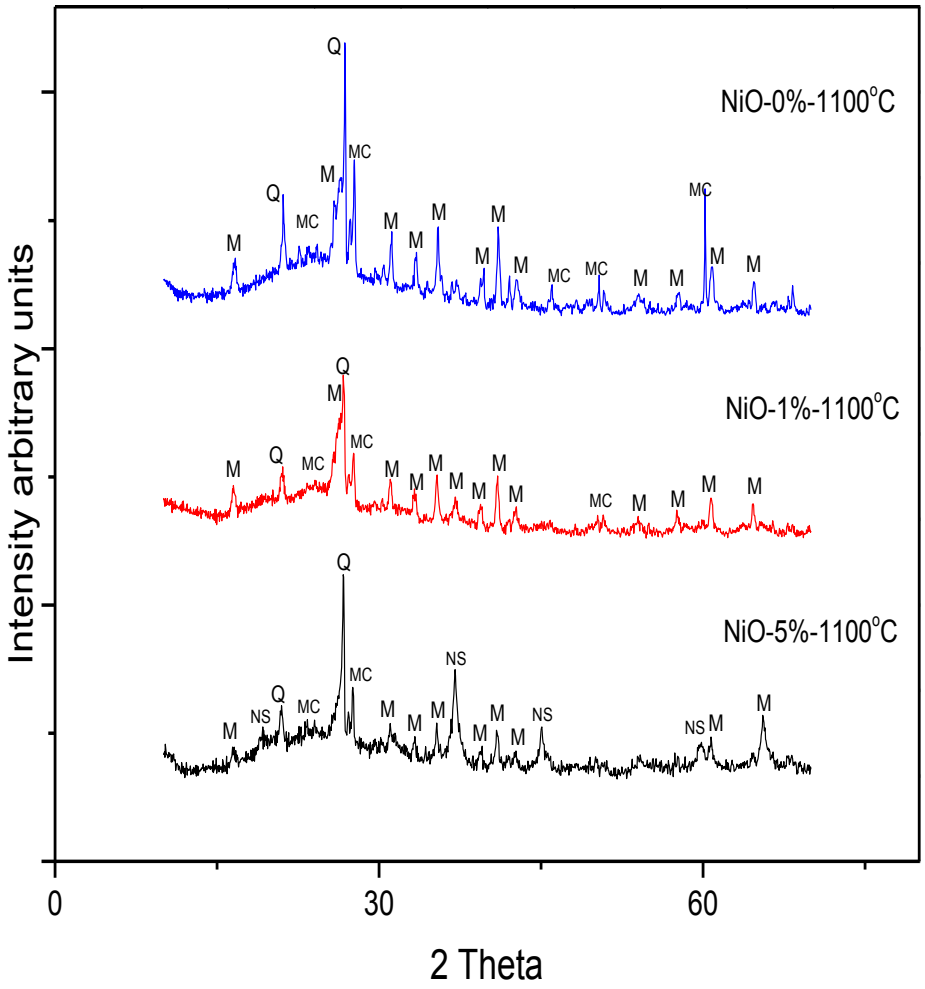
densification process in presence of glassy phase is assisted by the presence of these two additives. The effectiveness of CoO and NiO is so much prominent in the temperature range 1100- 1200^{o}C. At higher temperature 1300^{o}C, presence of this additive rather deteriorates the physical properties of the sample. At 1300^{o}C particularly in presence of higher amount of additive the viscosity of glassy phase decreased a large amount, which cause bloating action in the feldspathic region of these over fired body leading to pore formation and shrinkage reduction.



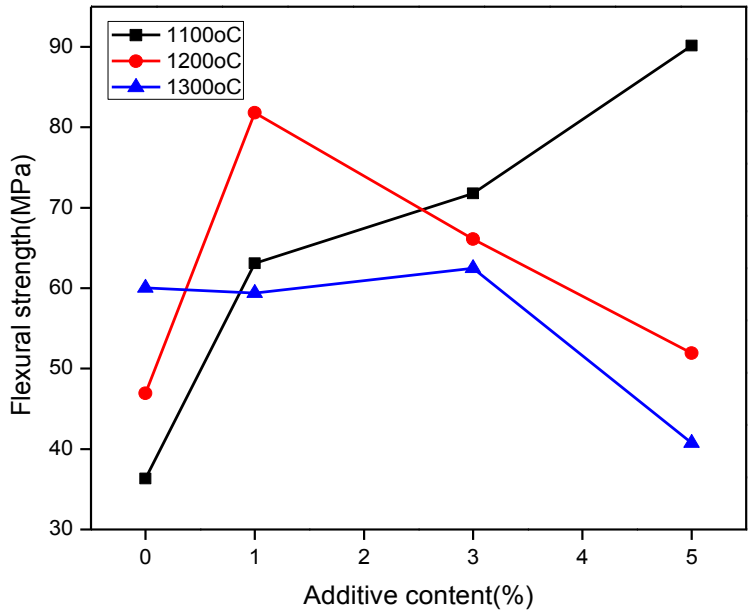
Figure; 4.2.5(a) XRD patterns of 1100^{o}C fired batches with and without CoO additive.

Figure 4.2.5(a) represents the XRD patterns of 1100^{o}C fired batches containing 0%, 1% and 5% CoO additive. In absence of CoO additive the main crystalline phases formed were mullite(M), quartz(Q) and microcline(MC), that indicates primary mullitization already occurred and microcline still remains in the crystalline form and its conversion into glassy form not yet finished. When CoO additive added only 1% then some of the microcline peaks disappeared, instead new mullite peaks appeared. So CoO helps in mullite formation which is an exothermic reaction that facilitate feldspar fusion. When higher amount CoO added, feldspar fusion almost completed. Only two microcline peaks were there along with mullite phase and a new phase cobalt aluminate (CA) appeared.

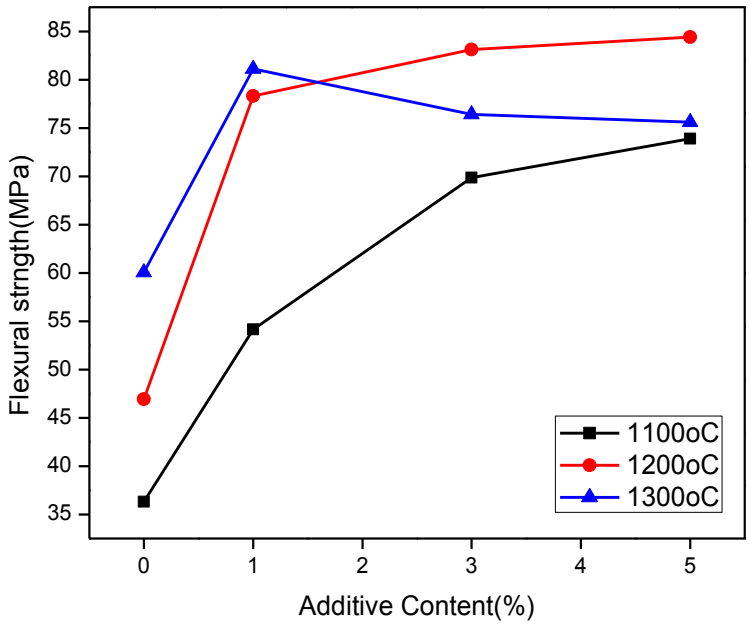
Figure 4.2.5(b) given below shows the XRD of 1100^{o}C fired batch in presence and absence of NiO. The main crystalline phases found were quartz(Q), mullite(M) and microcline(MC). In presence of 1% NiO some of the microcline phase disappear and other peak intensity decreased. Which indicated presence of NiO helps in feldspar dissolution, thus help in mullite phase formation. It is also supports by the increase in the intensity of mullite peaks which was found. In presence of higher percentage of NiO the mullite phase decreased, instead anther Ni-SiO_4(NS) phase was appeared. Here excess amount of NiO react with silicious glassy phase to form neutral silicate which affect the secondary mullitization process.



Figure; 4.2.5 (b) XRD patterns of 1100°C fired batches with and without NiO additive.



Figure; 4.2.6(a) Variation of Flexural strength with the amount of CoO additive added.



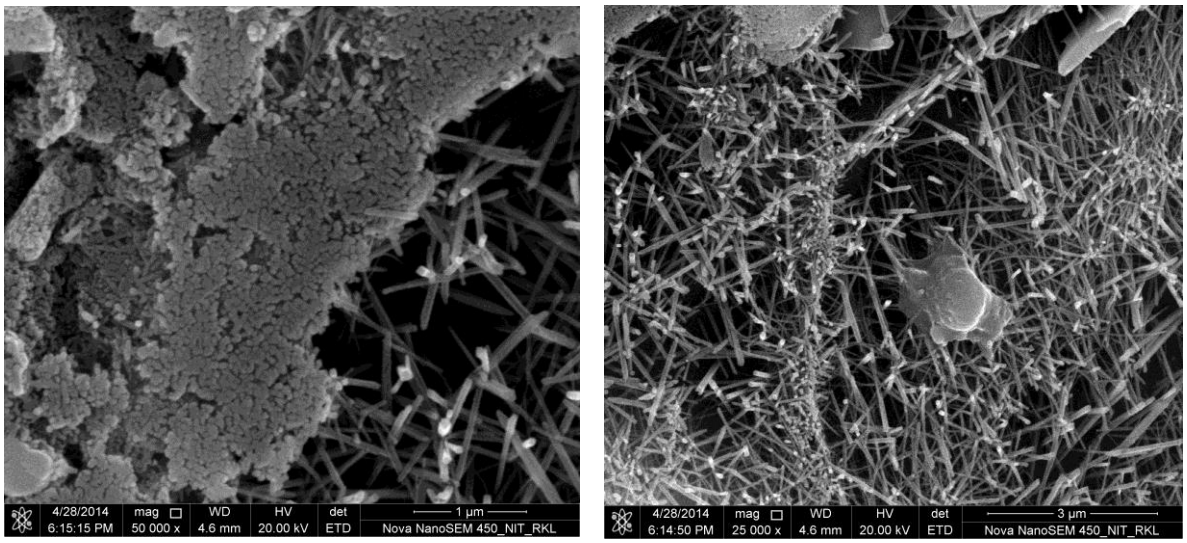
Figure; 4.2.6(b) Variation of Flexural strength with the amount of NiO additive added.

Figure 4.2.6(a) and 4.2.6(b) represent the variation of flexural strength with increasing percentage of additive at three different temperatures. At lower temperature 1100^{o}C strength increase occur in both NiO and CoO batches. For higher temperature 1200^{o}C strength enhancement show in presence of 1% CoO, for higher amounts of additive strength decreased. For NiO batch also at 1200^{o}C increase in strength with increase in additive amount is shown by the curve. At higher temperature the change in strength was only appreciable with 5% CoO batch, where the strength decreased. At 1300^{o}C from 0% - 1% NiO additive the strength increased, for higher amount of additive the change was not attractive. The reduction of viscosity of glassy phase in presence of CoO and NiO additive at lower temperature range enhances the sintering process, and the amount of mullite phase increased. There mullite are formed in a matrix of less viscosity, so they are needle shaped and interlocked properly. Thus helps in strength enhancement.

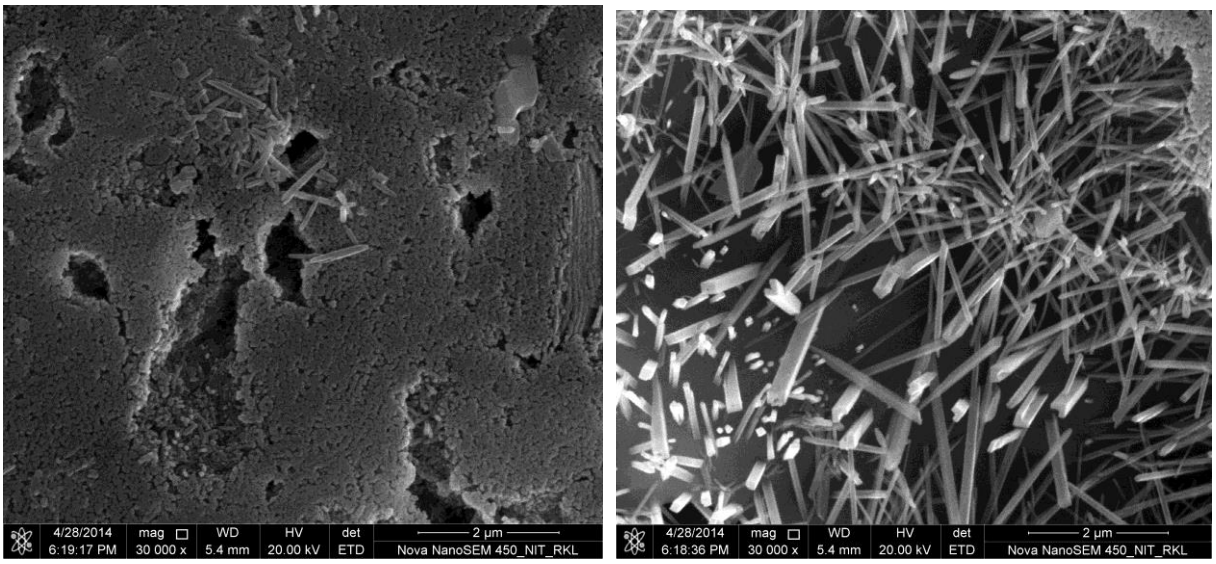
At 1300^{o}C and in presence of NiO and CoO additive, the matrix fluidity is maximum. Now the needle shaped type-III mullite started to encounter with other mullite crystals resulting growth inhibition in the longitudinal direction. And now the growth occurs in the transverse direction. Anisotropic grain growth is favored by first phase formation and then sintering. In presence of additive sintering is initiated at comparatively low temperature. So now the anisotropic grain growth under such strained condition is difficult.

In porcelain primary mullite was found at around 1000^{o}C from clay particles. This primary mullitization is not generally affected by the presence of mineralizers. [14] The secondary mullitization occur in a tri-axial composition by the reaction between clay and feldspar and this reaction is very much affected by the presence of mineralizers. At a temperature around 1100^{o}C after primary mullitization, feldspar gets fused and this fused mass starts to penetrate clay relicts and then secondary mullitization occurs. Mineralizer like CoO and NiO that are present in this

situation helps to reduce the viscosity of fused feldspar and clay relict. This ease the reaction between clay and feldspar and facilitate secondary mullitization. Because of this facilitated mullite formation in presence of 1% NiO and CoO additive, the physical properties are modified to a large extend at comparatively lower temperature.

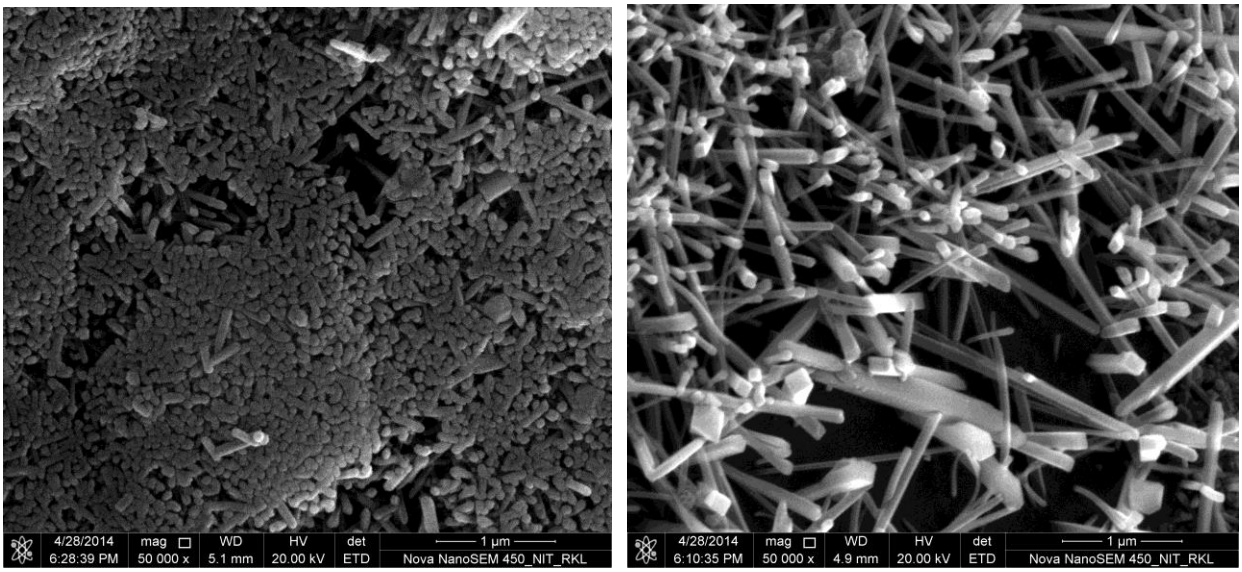


Figure; 4.2.7(a) and 4.2.7(b) FESEM images of 1% CoO batch fired at 1100°C.



Figure; 4.2.8(a) and 4.8(b) FESEM images of 5% CoO batch fired at 1100°C.

Figure 4.2.7(a), (b) and 4.2.8(a), (b) shows microstructures of 1% and 5% CoO additive containing batches fired at 1100^{o}C. From the figure it was found that for 1% CoO batch both primary and secondary mullite phase were present. Secondary mullite are needle shaped and properly interlocked, which is the reason for their higher strength, compared to the without additive batch. In presence of 1% CoO as the viscosity of glassy phase is less, so the anisotropic grain growth is favored which is the basic requirement for self-reinforcement. And this reinforcement upgrade the mechanical property of the ceramic. The microstructure of 5% CoO containing batch also show the presence of both primary and secondary mullite. The presence of higher amount of additive reduces the glass viscosity for which densification, pore removal and sintering is better. In both cases the presence of type-III mullite is clearly shown by the micrograph.



Figure; 4.2.9(a) FESEM inage1% NiO 1200^{o}C and 4.2.9(b) FESEM image of 5% NiO batch fired at 1200^{o}C.

Figure 4.2.9(a) and 4.2.9(b) represent microstructure of 1% and 5% NiO containing batches fired at 1200^{o}C. In the 1% NiO batch primary mullite along with needle shaped secondary mullite

are found. For 5% batch only secondary mullite with higher interlocking is found. Presence of higher amount of NiO, higher temperature like 1200^{o}C generates low viscosity glassy phase due to which physical and mechanical property improvement was noticed.

CHAPTER- V

SUMMARY AND CONCLUSIONS

CONCLUSIONS

Effect of transition metal oxides such as Cr_2O_3, CoO and NiO on the physico mechanical properties of tri- axial system was studied. Form the obtained results it was concluded that,

- In tri-axial systems containing clay, quartz and feldspar the different phase developments occurring during firing depends on the liquid phase formation from the melting of feldspar and quartz and followed by the dissolution and re-precipitation. Also viscosity of the melt depends on further nucleation and development of phases.
- Cr_2O_3 additive because of its refractory nature does not enhance any properties of the tri-axial system, whereas degradation properties were observed. Chromium containing batches were having increased porosity, lower Bulk density and strength with lacking mullite contents.
- CoO and NiO that are present in the body acts as a mineralizer, reduce the viscosity of glassy phase containing fused feldspar and clay relicts. This advances the interaction between clay and feldspar and facilitate secondary mullitization. When the viscosity of glassy melt is low because of higher additive content, anisotropic grain growth of mullite results.
- Hence transition metal oxides like CoO and NiO can be used as an additive for applications in different fields requiring higher strength and densities.

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